









# CHEMICAL REVIEWS

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# SYMPOSIUM ON COMPLEX INORGANIC COMPOUNDS<sup>1</sup>

## INTRODUCTION TO THE SYMPOSIUM

JOHN C. BAILAR, JR.

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*Received July 29, 1937*

The coördination theory was originally proposed to account for the peculiar stability and properties of the metal ammines. It was quickly seen, however, that the theory had many other applications, and through the passing years its implications have been extended to an ever-widening field. Sidgwick's (9) modernization of the theory in terms of electronic structure has greatly accelerated this trend in recent years. The tendency to form coördinate compounds is, indeed, one of the most fundamental properties of both organic and inorganic molecules. Morgan and Burstall's recent review of modern developments in inorganic chemistry (5) lists stable coördination compounds of nearly every element in the periodic table. The "complex" compounds studied by Werner and the other early workers are simple indeed compared with the coördinate molecules now under investigation. For example, the recent studies of Reihlen and his coworkers (7) have established the fact that the heavy metal cyanides are polynuclear substances of very high molecular weight, while the studies of Brintzinger and his associates (3) have shown that many of the common complex ions act as nuclei for "super-complex" ions.

The rapid growth of the field of coördination compounds and the great interest which the symposium<sup>2</sup> held in 1936 elicited made it seem wise to arrange another symposium this year. The first paper in this symposium—"The Volatile Metal Carbonyls"—is presented by Professor Arthur A. Blanchard of The Massachusetts Institute of Technology. He has studied these compounds for many years, and his researches have contributed greatly to our knowledge of them. In the second paper Dr. Harvey Diehl

<sup>1</sup> Held by the Division of Physical and Inorganic Chemistry at the Ninety-third Meeting of the American Chemical Society, Chapel Hill, North Carolina, April 14, 1937.

<sup>2</sup> The papers presented at the former symposium were the following: "The Hydrogen Bond and Coördination," by W. H. Rodebush (8); "The Acid-Base Properties of Complex Ions," by N. F. Hall (4); "The Stereochemistry of Complex Inorganic Compounds," by John C. Bailar, Jr. (1); and "Polyhalides," by H. S. Booth.

of Cornell University discusses "The Classification of Chelate Rings", a subject of enormous importance to analytical chemists as well as to those interested purely in the theory and mechanism of coordination.

Bjerrum (2) found in 1907 that heating basic chromic sulfate solutions caused polymerization, and advanced the theory of "olation", which has since been greatly extended. The studies of Professor A. W. Thomas and his students at Columbia University have indicated that colloidal oxide particles are really giant coordination molecules formed by "olation" and "oxolation", and are perhaps the most complex of all complex molecules. In the third paper of this symposium Professor T. H. Whitehead of the University of Georgia discusses "The Complex Compound Theory of Colloidal Oxides." Professor Whitehead was one of the first of Professor Thomas' students to work in this field, and has continued his work on the colloidal oxides since leaving Columbia University.

Many other phases of the chemistry of complex inorganic molecules remain for discussion at later symposia. Among the most interesting of these are the problem of the structure of poly acids, upon which the recent work of Pauling (6) has thrown great light, the coordination compounds of unsaturated organic molecules, the structure of minerals, and the preparation of insoluble, colored compounds which can serve as pigments. All of these subjects are now receiving much attention. There remain other phases of the chemistry of coordination compounds which have been explored but little; for example, stability relationships of complex inorganic compounds, stabilization of valences through coordination, and the separation of the naturally occurring amino acids by the use of complex inorganic ions as precipitants. These may at some time furnish topics for symposia.

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# THE VOLATILE METAL CARBONYLS<sup>1</sup>

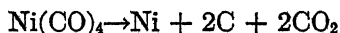
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*Received August 2, 1937*

The metal carbonyls constitute not only a most interesting but also a most unusual series of compounds. In fact, there is no other type of compound which has any close resemblance to the metal carbonyls. One of the most outstanding characteristics of the metal carbonyls, the reversibility of their formation, is possessed also by hydrates, ammoniates, and similar complexes, but it is only in the carbonyls that the central atom of the complex has the oxidation and reduction valence of zero.

Nickel carbonyl is, perhaps, the most typical of the carbonyls. If finely divided metallic nickel is prepared by heating nickel formate at the lowest possible temperature (below 200°C.), this active nickel will at room temperature and atmospheric pressure take up carbon monoxide as rapidly as it can be supplied, with the formation of nickel carbonyl,  $\text{Ni(CO)}_4$ . This is a colorless, very mobile liquid with a vapor pressure of one-third of an atmosphere at room temperature. When it is slowly heated, nickel carbonyl begins to decompose at about 60°C. into nickel (usually deposited on the walls as a brilliant mirror) and carbon monoxide; at higher temperature the decomposition is complete. These mirrors, if they are uncontaminated by traces of oxygen, will frequently disappear again in a stream of cold carbon monoxide. When it is heated suddenly, nickel carbonyl decomposes irreversibly with a rather mild detonation.



If the central atom of the metal carbonyl is regarded as zero valent, then the carbonyl group is also zero valent. Thus, this group in the metal carbonyls is of a totally different character from the carbonyl group in other carbon compounds, such as acetone and phosgene, where two primary valence bonds attach the carbonyl group to other parts of the molecule. Furthermore, carbonyl compounds of the latter type cannot be reversibly formed from carbon monoxide.

<sup>1</sup> Contribution No. 64 from the Research Laboratory of Inorganic Chemistry at The Massachusetts Institute of Technology.



Many of the metal carbonyls possess the surprising property of a high degree of volatility, as is shown in table 1.

Nitric oxide has a property similar to that of carbon monoxide of combining reversibly with metals, although this reversibility is often partly concealed, in that decomposition of the nitrosyls leads to a disproportionation of the liberated nitric oxide and a consequent formation of nitrate or nitrite of the metal. Very volatile hydrogen compounds of metal carbonyls have been prepared by indirect reactions; although these have not been synthesized directly, they break down very easily into hydrogen and

TABLE 1  
*Volatile carbonyls*

CARBONYL	MELTING POINT	VAPOR PRESSURE	TEMPERATURE AT WHICH IT BEGINS TO DECOMPOSE
	°C.	mm.	°C.
Ni(CO) <sub>4</sub> .....	-25	261 (at 15°C.)	60
Fe(CO) <sub>5</sub> .....	-21	15 (at 25°C.)	150
Ru(CO) <sub>5</sub> .....	-22	Very volatile	-15
Cr(CO) <sub>6</sub> .....	Sinters at 90	1 (at 48°C.)	130
Mo(CO) <sub>6</sub> .....	Sinters at 120	2 3 (at 55°C.)	150
W(CO) <sub>6</sub> .....	Sinters at 125	1.2 (at 67°C.)	150
[Co(CO) <sub>4</sub> ] <sub>2</sub> .....	50	0.07 (at 15°C.)	53

TABLE 2  
*Volatile nitrosyl carbonyls and carbonyl hydrides*

COMPOUND	MELTING POINT	VAPOR PRESSURE
	°C.	mm.
Co(CO) <sub>2</sub> NO.....	-11	56 (at 16°C.)
Fe(CO) <sub>2</sub> (NO) <sub>2</sub> .....	+18	4.5 (at 0°C.)
Co(CO) <sub>4</sub> H.....	-33	High
Fe(CO) <sub>4</sub> H <sub>2</sub> .....	-70	11 (at -10°C.)

non-volatile carbonyls. Volatile nitrosyl and hydrogen compounds are listed in table 2.

Vapor density measurements have shown all of the volatile carbonyls of tables 1 and 2, except cobalt tetracarbonyl, to be monomeric. The cobalt tetracarbonyl is dimeric. It is placed in table 1 to show the transition between the volatile and non-volatile carbonyls. Actually, it can be sublimed in a vacuum or, better, in a current of carbon monoxide. Several of the carbonyls listed in table 3 as non-volatile can be sublimed with nearly the same ease as cobalt tetracarbonyl. The pure nitrosyls in this

list appear to be completely non-volatile, and their degree of polymerization is not known. They do, however, decompose and give fumes with moist air. The molecular weights of these non-volatile carbonyls, with the exception of ruthenium tetracarbonyl, have been determined by the freezing-point method in indifferent solvents, and the degree of polymerization shown in the formulas has been found. Ruthenium tetracarbonyl

TABLE 3  
*Non-volatile carbonyls and nitrosyls*

NON-VOLATILE CARBONYLS			NON-VOLATILE NITROSYLS	
$\text{Fe}_2(\text{CO})_9$ $[\text{Fe}(\text{CO})_4]_3$	$[\text{Co}(\text{CO})_4]_2$ $[\text{Co}(\text{CO})_3]_4$	$\text{Ru}_2(\text{CO})_9$ $[\text{Ru}(\text{CO})_4]_n$	$\text{Fe}(\text{NO})_4$	$\text{Ru}(\text{NO})_{4-5}$

TABLE 4  
*Other non-volatile carbonyls*

CARBONYLS OF METAL HALIDES	CARBONYLS CONTAINING PYRIDINE, ETHYLENEDIAMINE, OR o-PHENANTHROLINE	COMPOUNDS IN WHICH HYDROGEN OF CARBONYL HYDRIDES HAS BEEN REPLACED BY A METAL
$\text{PtCl}_2(\text{CO})$ $\text{PtCl}_2(\text{CO})_2$ $(\text{PtCl}_2)_2(\text{CO})_3$ $\text{RuI}_2(\text{CO})_2$ $\text{RhCl}_2 \cdot \text{RhO}(\text{CO})_3$ $\text{IrCl}_2(\text{CO})_2$ $\text{PdCl}_2\text{CO}$ $\text{OsCl}_2(\text{CO})_3$ $\text{Fe}(\text{CO})_4\text{I}_2$ $\text{Fe}(\text{CO})_5\text{I}_2$	$\text{Fe}_2(\text{CO})_4\text{py}_3^*$ $\text{Fe}(\text{CO})_2(\text{CN})_2\text{py}$ $\text{Fe}(\text{CO})_4\text{en}_2\text{I}_2$ $\text{Fe}(\text{CO})_3\text{py}_2\text{I}_2$ $\text{Fe}(\text{CO})_2(o\text{-phthr})_2\text{I}_2$ $\text{Fe}(\text{CO})_2(o\text{-phthr})\text{I}_2$ $\text{Fe}(\text{CO})\text{py}_2\text{I}_2$ $\text{W}(\text{CO})_4(o\text{-phthr})$ $\text{Cr}(\text{CO})_4\text{py}_2$ $\text{Cr}_2(\text{CO})_7\text{py}_5$ $\text{Cr}(\text{CO})_5\text{py}_3$ $\text{Co}_2(\text{CO})_8\text{py}_4$ $\text{Co}(\text{CO})_3(o\text{-phthr})$ $\text{Ni}_2(\text{CO})_4\text{py}$ $\text{Ni}(\text{CO})_3\text{py}$ $\text{Ni}_2(\text{CO})_5\text{py}_2$ $\text{Ni}(\text{CO})_2(o\text{-phthr})$	$\text{Fe}(\text{CO})_4\text{Hg}$ $\text{Fe}(\text{CO})_4\text{Hg}_2\text{Cl}_2$ $[\text{Co}(\text{CO})_4]_2\text{Hg}$ $\text{Co}(\text{CO})_4\text{Ag}$ $\text{KCo}(\text{CO})_4$ $\text{K}_2\text{Fe}(\text{CO})_4$ $\text{K}_3[\text{Fe}(\text{CN})_5\text{CO}]$

\* py = pyridine; en = ethylenediamine; o-phthr = o-phenanthroline.

may be expected to have the same polymerization as the trimeric iron tetracarbonyl.

In addition to the volatile metal carbonyls,—and under this title let us include always the volatile nitrosyl carbonyls and carbonyl hydrides,—there have been prepared a bewildering number of non-volatile complexes which contain carbonyl or nitrosyl groups or both. In table 4 is shown a typical, but far from complete, list of such compounds.

In the first column of table 4 appear carbonyls of metal halides. One of the carbonyls of platinous chloride is so stable that it can be sublimed like cobalt tetracarbonyl. The iodides  $\text{Fe}(\text{CO})_4\text{I}_2$  and  $\text{Fe}(\text{CO})_5\text{I}_2$  are obtained only at low temperatures by the addition of iodine to anhydrous iron carbonyl. Addition of water causes immediate decomposition into ferrous iodide and carbon monoxide.

When the carbonyls and nitrosyl carbonyls are treated with such complex-forming substances as ammonia, pyridine (py), ethylenediamine (en), *o*-phenanthroline (*o*-phthr), etc., there is usually a rapid evolution of carbon monoxide. The formulas given in the second column show the composition of some of the substances that can be crystallized at various temperatures. It is particularly noteworthy that in no case has there been a complete displacement of the carbonyl groups to give a zero valent complex of the metal.

In the third column are shown compounds in which the hydrogen of the carbonyl hydrides has been replaced by a metal. The heavy metal compounds are insoluble in water but soluble in organic solvents. The alkali and alkaline-earth metal compounds are soluble in water and appear to bear the salt-to-acid relation to the corresponding hydrides.

The definitions of the terms "valence", "cohesion", and "chemical affinity" have never been very well standardized, but according to the most usual understanding of these concepts, they all arise from the same source, namely, the field of the atoms and molecules and, in fact, the field of the electrons and nuclei within the atoms. With the inert gases the field of the electrons and the field of the nucleus are mutually neutralized, and the lack of field external to the atom explains the lack of chemical affinity and the zero valence of the inert gases.

All other atoms possess external fields. Where definite groups of atoms can form in which the fields of the different atoms are mutually neutralized, there is little cohesion between the molecules and the compounds are volatile.

Through the position of the so-called valence electrons, the field between two atoms may be localized into what is regarded as a valence bond.

Although a study of the chemical composition of the volatile carbonyls may not furnish a definite decision as to the location of the chemical bonds, nevertheless the number of possible locations is limited. On the other hand, in non-volatile carbonyls in which the cohesion is continuous and not restricted within small groups of atoms, the problem of locating the position of the bonds becomes more complicated.

The importance and the theoretical significance of the large array of non-volatile mixed carbonyls should not be in any way minimized; nevertheless the present study concerns itself principally with the volatile carbonyls

and the property of volatility. First, space does not allow the complete field to be covered, and second, the greater simplicity of the volatile compounds offers a greater possibility of understanding the nature and position of the valence bonds.

No attempt is made in this paper to discuss the significance of the magnetic and dielectric properties of the carbonyls or of the x-ray or electron diffraction, or the light absorption studies. Most interesting and important data have been obtained from these studies, and these must finally be coordinated before the nature of the carbonyls is completely understood.

We owe to Sidgwick (88, 82) the useful term "effective atomic number", which is applied to the central atom of complexes. This is the total number of electrons existing within the sphere of the atom in the complex, and embraces both those electrons originally belonging to the atom itself and also the electrons donated by the surrounding groups. The implication

TABLE 5  
*Effective atomic number of central atom*

VOLATILE CARBONYL	EFFECTIVE ATOMIC NUMBER OF CENTRAL ATOM	INERT GAS HAVING SAME ATOMIC NUMBER
Ni(CO) <sub>4</sub> . . . . .	28 + 8 = 36	Krypton
Fe(CO) <sub>5</sub> . . . . .	26 + 10 = 36	Krypton
Ru(CO) <sub>5</sub> . . . . .	44 + 10 = 54	Xenon
Cr(CO) <sub>6</sub> . . . . .	24 + 12 = 36	Krypton
Mo(CO) <sub>6</sub> . . . . .	42 + 12 = 54	Xenon
W(CO) <sub>6</sub> . . . . .	74 + 12 = 86	Radon

of this term is that the stability of the complex is dependent on the symmetry of the arrangement of the electron groups within the central atom, and particularly, that when the effective atomic number is equal to the atomic number of one of the inert gases, this will be reflected in the self-contained character of the central atom. If, furthermore, the field of the surrounding groups is self-contained except where it mutually neutralizes that of the central atom, then the whole complex will be self-contained, and if the net charge of the whole complex is zero, the complex will be volatile.

If it is postulated that each carbonyl group donates two electrons to the central atom it is seen in table 5 that the effective atomic number of the central atom in each of the volatile carbonyls is identical with the atomic number of an inert gas.

Since nickel carbonyl possesses the most self-contained field and of all the carbonyls is the least subject to rearrangement additions or substitutions, other than a complete dissociation into nickel and carbon monoxide, we may well first give our attention to its structure. There can be little

doubt that nickel is the central atom of the complex, and that it is surrounded by four coördinately bound and symmetrically placed carbonyl groups. If we assume that each carbonyl group donates two electrons to the central atom, the effective atomic number of the nickel becomes  $28 + (4 \times 2) = 36$ , which is the atomic number of krypton.

Cobalt lacks one electron (82) and iron two electrons to give a structure of the same pattern. But the nitrosyl group has a structure similar to that of the carbonyl group and it possesses one more electron. Thus, in the nitrosyl carbonyls  $\text{Co}(\text{CO})_2\text{NO}$  and  $\text{Fe}(\text{CO})_2(\text{NO})_2$  we can have the effective atomic number of 36 for the central atom and the same electron pattern for the whole molecule. In the carbonyl hydrides  $\text{Co}(\text{CO})_4\text{H}$  and  $\text{Fe}(\text{CO})_4\text{H}_2$ , the electrons necessary to complete the pattern are furnished by the hydrogen atoms.

If it is postulated that the nitrosyl group donates three electrons and each hydrogen one electron, we see in table 6 that in the volatile nitrosyl

TABLE 6  
*Effective atomic number of the central atom*

CARBONYL	EFFECTIVE ATOMIC NUMBER OF CENTRAL ATOM
$\text{Co}(\text{CO})_2\text{NO}$ .....	$27 + 6 + 3 = 36$
$\text{Co}(\text{CO})_4\text{H}$ .....	$27 + 8 + 1 = 36$
$\text{Fe}(\text{CO})_2(\text{NO})_2$ .....	$26 + 4 + 6 = 36$
$\text{Fe}(\text{CO})_4\text{H}_2$ .....	$26 + 8 + 2 = 36$

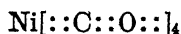
carbonyls and carbonyl hydrides the effective atomic number of the central atom is in each case equal to that of krypton.

There can be little doubt then that the basic electron pattern of the highly volatile carbonyl hydrides and nitrosyl carbonyls is the same as that of nickel carbonyl. The center of the positive charges is not, however, coincident with the center of the electron pattern as in nickel carbonyl, and in consequence these modified tetracarbonyls display an electric moment.

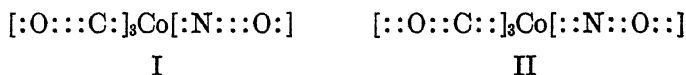
The most favored electron pattern of carbon monoxide  $:\text{C}:::\text{O}:$  shows three electron pairs held in common. Two alternatives present themselves by which the nickel complex may be formed: (I) Without alteration of the triple bond between the carbon and oxygen atoms the lone pair of the carbon atom may enter the shell of the nickel atom:



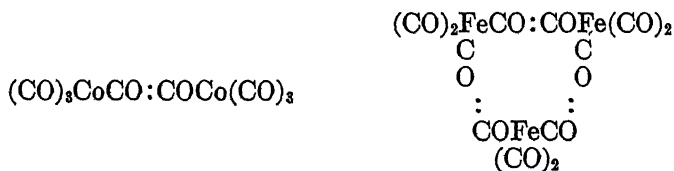
(II) This lone pair may be donated to the nickel shell and at the same time the nickel may donate two electrons with a consequent shift of electrons to give the pattern



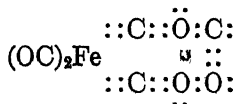
If the structure of nitric oxide is identical with that of carbon monoxide except for an additional imprisoned electron, the extra electron would be transferred completely to the shell of the central atom in nitrosyl formation and the pattern would then be identical with that of the carbonyl.



Evidently the coordination number is four in the cases already cited. There must be an inherent tendency among the carbonyls and nitrosyls to acquire the symmetry of this coordinate grouping. Indeed, it is probably the tendency to acquire this symmetry which is reflected in the prevalence of the tetracarbonyls among the non-volatile (or little volatile) carbonyls  $[\text{Co}(\text{CO})_4]_2$ ,  $[\text{Fe}(\text{CO})_4]_3$ , and  $[\text{Ru}(\text{CO})_4]_n$ . If the polymerization is due to a linking of two carbonyl groups, each electron pair held in common will free two electrons to increase the effective atomic number of the central atoms.



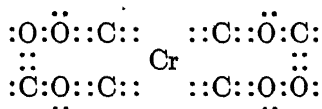
In iron pentacarbonyl if structure I is the correct carbonyl metal linkage the five carbonyl groups are bound directly to the central atom and the coördination number is five. If the carbonyl groups are bound in the pattern shown in II, only four would be bound to the central atom and the fifth would bridge across two of those directly bound:



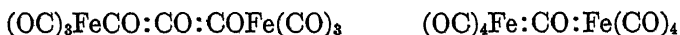
The number of electrons saved by this bridge and thus passed along to bring the effective atomic number of the central atom up to 36 is two. If a similar bridge were formed according to pattern I the number of electrons saved for the central atom would be four, which would raise the effective atomic number to 38.

According to structure I chromium hexacarbonyl would contain six carbonyl groups directly bound to the central atom, and the coordination number would be six. According to structure II the electron pattern of

nickel carbonyl with a coördination number of four would prevail and there would be two CO bridges:

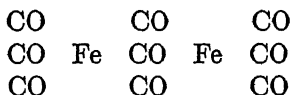


In the enneacarbonyls  $\text{Fe}_2(\text{CO})_9$  and  $\text{Ru}_2(\text{CO})_9$  there is obviously a CO bridge between the two metal atoms and the coördination number may be either four or five, according to whether the bridging CO joins two of the carbonyl groups or joins the two metal atoms directly.



In either case structure I alone will allow the correct saving of electrons to bring the effective atomic number of iron to 36 or of ruthenium to 54.

In view of the low volatility, however, perhaps it is not necessary to make the effective atomic number of the iron equal to that of an inert gas. Hieber gives the probable structure as



with three CO bridges and the coördination number of six for the iron atoms. Such a structure he believes to be supported by the x-ray diffraction studies of the substance (Brill (7)).

#### PREPARATION OF CARBONYLS

1. All of the metal carbonyls, except that of chromium, have been prepared by direct combination of the metal with carbon monoxide. High pressures and somewhat elevated temperatures are often employed.

2. Carbonyls also are prepared from metal salts and carbon monoxide in the presence of quite a variety of combinations of reagents. Always, however, one essential function of the reagents is to effect the reduction of the metal. In the presence of strong alkalies the carbon monoxide may also, itself, act as the reducing agent, the fixation of the carbon dioxide by the alkali greatly enhancing the reducing power of the carbon monoxide.

#### NICKEL CARBONYL, $\text{Ni}(\text{CO})_4$

##### *Preparation of nickel carbonyl*

*Direct synthesis.* Nickel carbonyl is undoubtedly most easily prepared by direct synthesis, although certain conditions have to be scrupulously observed to ensure the success of the process. Compact pieces of nickel

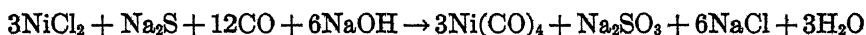
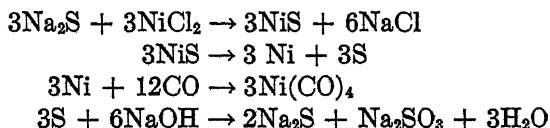
that have been exposed to air are practically without action upon carbon monoxide. Finely divided, freshly reduced nickel combines readily with carbon monoxide at room temperature and atmospheric pressure. In the Mond process for the commercial production of nickel from its ores, the ore is converted to the oxide, the oxide is reduced with producer gas at an elevated temperature, the nickel is subjected to producer gas at a lower temperature, the nickel carbonyl vapor entrained in the producer gas is decomposed with deposition of nickel in a heated chamber, and the producer gas is again ready to repeat the cycle.

For the laboratory preparation of nickel carbonyl the best results are obtained if commercial nickel formate is reduced in hydrogen at the lowest possible temperature, best below 200°C. After cooling, this reduced nickel absorbs carbon monoxide with great avidity, and if this gas is supplied rapidly a steady stream of liquid nickel carbonyl will flow from the outlet of the reaction vessel. The least trace of oxygen poisons the nickel so that it ceases to react readily, but strangely enough a few bubbles of hydrogen sulfide revivify the nickel (74).

*Preparation from nickel salts.* The formation of nickel carbonyl has been reported in several wet reactions with nickel salts, but none of these methods can compete with the dry synthesis as a method of preparation.

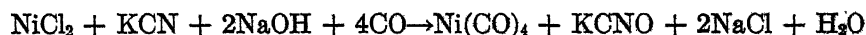
Manchot and Gall (67) observed that nickel carbonyl is formed when carbon monoxide is passed into a suspension of a nickel salt in caustic alkali and alkali sulfide.

Windsor and Blanchard (91) studied the mechanism of this process and reached the conclusion that in the presence of a sulfur-removing reagent the potential of the nickel in nickel sulfide could rise to the point of carbonyl formation.



The summation in the last equation shows that nickel is reduced from +2 valence to zero valence at the expense of sulfur, which is oxidized from -2 to +4.

Blanchard, Rafter, and Adams (5) found that cyanide is fully as effective as sulfide in promoting carbonyl formation in an alkaline suspension of a nickel salt. They propose a mechanism analogous to that for the sulfide method, similar steps being summarized in the over-all equation:



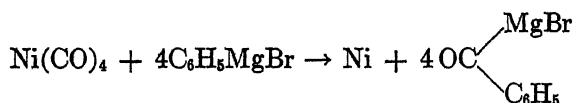


It should be stated that in the cyanide method, as indeed in the sulfide method, it is extremely probable that the intermediate formation of complex ions containing the carbonyl group plays an important part in facilitating the over-all result indicated by the equations.

Job and Reich noted that such unsaturated compounds as ethylene (53) and carbon monoxide (52) alone failed to react with Grignard reagents, but that in the presence of certain metal salts a reaction took place. In the case of nickel chloride it was found that nickel carbonyl could be detected, but no considerable amount was ever obtained. The Grignard reagent reduces the nickel salt as follows:



The reduced nickel combines with carbon monoxide to give nickel carbonyl, but the latter is very reactive toward the Grignard reagent, the equation



probably indicating the first step of a train of reactions. The nickel thus set free again takes up carbon monoxide to form nickel carbonyl. Thus an equilibrium concentration of nickel carbonyl is maintained, depending on the relative rates of its formation and its reaction with the Grignard reagent. At any time that the main process is stopped by hydrolysis of the Grignard reagent, only this equilibrium quantity of nickel carbonyl is obtainable from the mixture.

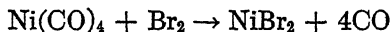
With respect to nickel carbonyl, this method of formation is of theoretical interest only. However, with chromium, molybdenum, and tungsten carbonyls it is the only practicable method of preparation; in fact, with chromium carbonyl it is the only method of formation that has been discovered.

#### *Behavior of nickel carbonyl*

Nickel carbonyl is soluble in, in fact, completely miscible with, organic solvents in general. It is not markedly soluble in water. It is without action with aqueous acids and alkalies.

When nickel carbonyl is formed from nickel and carbon monoxide, the latter substances suffer a most complete change of their physical properties, but only a very slight change of chemical properties. In fact, some of the chemical properties which they exhibit in the free state seem to be enhanced by their combination in the nickel carbonyl.

Nickel carbonyl reacts vigorously and quantitatively with bromine



the reaction being applicable to gas analytical procedure.

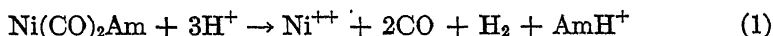
It reacts with the other halogens, with oxygen, and with sulfur in similar fashion, the nickel giving halide, oxide (hydroxide), and sulfide, respectively, and the carbon monoxide remaining free. Nickel carbonyl reacts slowly with oxygen, either dry or in the presence of water. Various observers have reported products which appear as crusts or deposits of the most varied appearance and composition. Berthelot (3) gives a composition  $\text{C}_2\text{O}_3\text{Ni}_3 \cdot 10\text{H}_2\text{O}$ ; Lenher and Loos (56),  $\text{Ni(CO)}_4 \cdot \text{Ni(OH)}_2 \cdot 4\text{H}_2\text{O}$ ; Thorne (90), a basic carbonate of nickel. These variable results apparently arise from the fact that nickel carbonyl is so volatile that during the long period of the reaction most of it escapes, even through water seals. Carbon dioxide of the air enters during the period to form carbonate. Blanchard and Gilliland (4) found that the oxidation product contained about 4 equivalents of formate per 100 equivalents of nickel. When the oxidation took place in a sealed vessel containing nickel carbonyl, water, and oxygen, after several weeks the residual gases consisted of carbon monoxide and unused oxygen and nickel carbonyl vapor, with no trace of carbon dioxide. The light green residue dissolved completely in dilute acid without trace of effervescence. It thus consisted solely of nickelous hydroxide and a little nickel formate but no nickel carbonate. The presence of formate is accounted for by the slow hydration of carbon monoxide to formic acid under the catalytic effect of the nickel carbonyl.

In contrast to the halogens, etc., which react only with the nickel, Grignard reagents act solely upon the carbon monoxide of the nickel carbonyl, and leave the nickel uncombined as a jet-black residue. Grignard reagents are as a rule without action on carbon monoxide alone, but react vigorously with the carbon monoxide of nickel carbonyl. This reaction has proved of great value in the study of Grignard syntheses from carbon monoxide; in fact, it has been found that a very small amount of nickel carbonyl is sufficient to effect such syntheses, the nickel acting as a carrier for the carbon monoxide (19).

The nickelous ion forms complexes with many amines, for example,  $[\text{Ni(NH}_3)_4]^{++}$ . Nickel carbonyl is the corresponding complex of zero valent nickel. No unmixed amine complexes of zero valent nickel are known, but several mixed amine carbonyl complexes are on record. When nickel carbonyl is treated with pyridine a slow effervescence is noted; removal of the carbon monoxide by pumping allows the reaction to proceed more fully, and finally it is possible to obtain crystallized products. Hieber, Mühlbauer, and Ehman (35) have identified three such prod-

ucts of the compositions  $\text{Ni}_2(\text{CO})_4\text{py}$ ,  $\text{Ni}(\text{CO})_2\text{py}$ , and  $\text{Ni}_2(\text{CO})_3\text{py}_2$ ; with 2-phenanthroline these authors have obtained the much more stable compound  $\text{Ni}(\text{CO})_2(o\text{-phthr})$ , in the form of ruby-red needles as much as 1 cm. long.

The behavior of these mixed carbonyl amine complexes with acids is of interest, and particularly so when comparison is made with the behavior of similar cobalt and iron complexes. If we allow Am to stand for the amine part of the complex, the reactions shown in equations 1 and 2 take place



with equation 1 predominating. In the unsubstituted nickel carbonyl complex the nickel does not enter into reaction with hydrogen ions.

#### *Nickel carbonyl and oxides of nitrogen*

The behavior of nickel carbonyl with oxides of nitrogen has recently (1936) been studied by Frazer and Trout (14). They find that nitrogen dioxide,  $\text{NO}_2$ , reacts exothermically even at a temperature as low as  $-78^\circ\text{C}.$ ; as much as 98 per cent of the carbon monoxide of the carbonyl and a small amount of carbon dioxide are found in the gaseous products. The solid product contains all of the nickel and appears to be a mixture of nitrate and nitrite in about the ratio of 3:1.

Nitrogen trioxide,  $\text{N}_2\text{O}_3$ , reacts similarly to the dioxide.

Nitric oxide,  $\text{NO}$ , reacts with liquid nickel carbonyl from  $-11^\circ$  to  $0^\circ\text{C}.$  to form a blue gelatinous solid product, which becomes almost white when excess of nickel carbonyl is removed. At room temperature bronze to olive-green deposits are obtained. These solid products are insoluble in water, but soluble in dilute sulfuric acid with evolution of red fumes. The analyses of the solid product are very variable, but practically all of the original carbon monoxide and a small amount of carbon dioxide are found in the gaseous products.

Nitrous oxide,  $\text{N}_2\text{O}$ , does not undergo any slow reaction with nickel carbonyl. The gas mixture explodes when ignited with a gas flame.

A green solid is obtained when a solution of nickel carbonyl in not anhydrous methyl alcohol is treated with nitric oxide. This substance is stable in air. Reihlen (83, 84) gives its composition as  $\text{NO} \cdot \text{NiOH} \cdot \text{OCH}_3 + \text{CH}_3\text{OH}$ . On the other hand, Anderson (2) gives its composition as  $\text{N}_2\text{O}_2 \cdot \text{Ni}(\text{OH})_2 + 4\text{CH}_3\text{OH}$ .

There still appears to be much uncertainty as to the nature of the nitrosyl compounds of nickel, but it is at least significant that no volatile nitrosyl or nitrosyl carbonyl has been discovered.

## COBALT CARBONYLS

*Preparation of cobalt carbonyls*

*Direct synthesis.* Finely divided cobalt (pumice soaked with cobalt salt solution and reduced in hydrogen at a low temperature) reacts a little with carbon monoxide, a trace of vapor being entrained which gives a faint cobalt mirror in a heated tube. When this cobalt is treated with a mixture of carbon monoxide and nitric oxide, the volatile cobalt nitrosyl carbonyl,  $\text{Co}(\text{CO})_3\text{NO}$ , is produced rather freely (5).

*Cyanide method.* An alkaline suspension of cobalt cyanide absorbs a considerable amount of carbon monoxide, but no identifiable carbonyl can be isolated, either as a vapor or by extraction with solvents. However, the moment nitric oxide is introduced the apparatus becomes filled with the deep yellow-brown vapor of cobalt nitrosyl carbonyl. This is a very serviceable method of preparation of the cobalt nitrosyl carbonyl (5).

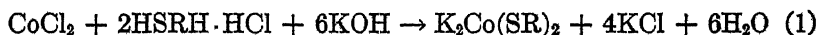
*Cysteine method: preparation of cobalt tetracarbonyl hydride.* Schubert (86), in making a study of the absorption of carbon monoxide by the cysteine complexes of cobalt and iron, found that with iron the potassium and sodium salts of the carbonyl complex could be isolated,



and also the free acid,



With cobalt, although similar complexes may represent intermediate stages, they could not be isolated; a disproportionation of the cobalt took place with formation of a cysteine complex of trivalent cobalt and a carbonyl complex containing no cysteine. Acidification of the latter complex caused separation of cobalt tetracarbonyl. Schubert worked out the following reactions (in the equations R stands for the part of the formula of cysteine,  $\text{HS}[-\text{CH}_2\text{CHNH}_2\text{COO}-]\text{H}$ , enclosed in brackets):



Equation 1 shows the formation of the cobaltous cysteinate complex.

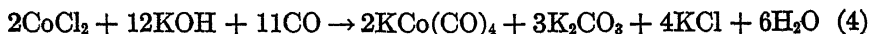


Reaction 2 takes place in moderately concentrated alkali and shows the disproportionation of the cobalt into a cobaltic cysteine complex and the carbonyl complex  $\text{HCo}(\text{CO})_4$ , which contains no cysteine.



Reaction 3 takes place in concentrated alkali solution and shows the oxidation of carbon monoxide to a carbonate and the reduction of the trivalent cobalt to the same carbonyl cobalt complex. The validity of these reactions was tested by very careful analysis. In particular, existence of the hydride  $\text{HCo}(\text{CO})_4$  was confirmed by the precipitation and analysis of both the mercuric and silver salts,  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and  $\text{AgCo}(\text{CO})_4$ .

Coleman and Blanchard (10), in seeking improved methods of preparing cobalt nitrosyl carbonyl, tried the use of cysteine. They first noted that consolidation of the three equations given by Schubert gave



according to which all of the cysteine is regenerated and a part of the carbon monoxide acts as the reducing agent.

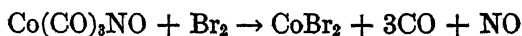
Actually they found that no absorption of carbon monoxide at all takes place in the absence of cysteine; nevertheless a small amount of cysteine brings about the absorption of a much larger proportion of carbon monoxide than shown in equations 2 and 3. In fact, they found rather more carbon monoxide absorbed than demanded by equation 4 on the basis of the cobaltous salt taken.

They found that in contrast to the alkaline cobaltous cyanide solution saturated with carbon monoxide, this alkaline cysteine solution did not yield any cobalt nitrosyl carbonyl upon treatment with nitric oxide. After acidifying, however, the case was quite different (see later). The immediate effect of acidification (without nitric oxide) was to liberate the hydride  $\text{HCo}(\text{CO})_4$ .

*Preparation of cobalt carbonyl hydride.* Coleman and Blanchard found that acidification of the solution described above (containing the salt  $\text{KCo}(\text{CO})_4$ ) produced effervescence (carbon dioxide). In agreement with Schubert they observed that the escaping gases had an almost intolerably vile odor. They swept the acidified solution with carbon monoxide and passed the entrained gases through phosphorus pentoxide and then through a trap immersed in solid carbon dioxide and alcohol, and obtained a light yellow crystalline solid. This substance had a perfectly sharp melting point at about  $-33^\circ\text{C}$ . It gave a clear, straw-yellow liquid. After being several times resolidified and remelted the substance began to acquire a reddish-brown color, and when it approached room temperature it effervesced strongly and changed to a dark colored solid. This residue was shown to be cobalt tetracarbonyl,  $[\text{Co}(\text{CO})_4]_2$ , and the gas which escaped was found to be hydrogen. The vapor which condensed to the light yellow solid was the hydride,  $\text{HCo}(\text{CO})_4$ . In the best run an amount of hydride was obtained which corresponded to 26 per cent of the cobalt taken.

*Preparation of cobalt nitrosyl carbonyl.* If, after acidification of the alkaline solution in the cysteine method, the sweeping with carbon monoxide is withheld for sometime, a black scum of cobalt tetracarbonyl rises to the surface. Then on introducing nitric oxide the shaking vessel becomes filled with reddish-brown vapors. These were swept with nitric oxide through phosphorus pentoxide into a trap in solid carbon dioxide and alcohol. Light yellow crystalline cobalt nitrosyl carbonyl was obtained. After several days with occasional sweeping the total yield of cobalt nitrosyl carbonyl, based on the cobalt salt taken, was 54 per cent.

Cobalt nitrosyl carbonyl has been found to react quantitatively with bromine.



The escape of free nitric oxide as well as carbon monoxide tends to support the postulate that the nitrosyl and carbonyl groups function similarly in the complex (10, 25).

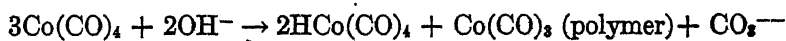
*Other assistants in the preparation of cobalt carbonyls.* Coleman and Blanchard found many other substances besides sulfide, cyanide, and cysteine which would promote the absorption of carbon monoxide by alkaline cobalt salt solution. The most effective of these proved to be tartaric acid and, although this did not cause as rapid an absorption as did cysteine, it was employed in the preparation of batches of both the carbonyl hydride and the nitrosyl carbonyl.

#### *Properties of cobalt tetracarbonyl*

Cobalt tetracarbonyl usually is obtained as a dark colored solid, but when it is entirely pure it exists as yellow crystals. Its molecular weight, as determined by the freezing-point method in benzene and also in iron pentacarbonyl, gives it the dimeric formula  $[\text{Co(CO)}_4]_2$  (35).

It melts at  $51^\circ\text{C}$ .; slightly above this temperature it begins to decompose, giving off carbon monoxide and leaving a residue of cobalt tricarbonyl. The latter is sparingly soluble in benzene and pentane, and can be purified by recrystallization from these solvents. It consists of pitch-black glistening crystals. By the freezing-point method in iron pentacarbonyl it is shown to have the tetrameric formula  $[\text{Co(CO)}_3]_4$ .

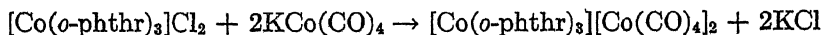
*Behavior with alkalis.* According to Hieber and Schulten (40, 41) cobalt tetracarbonyl reacts with strong bases as follows:



with weak bases, e.g., ammonia, as follows:



The presence of the hydride was confirmed by the addition of ammoniacal silver nitrate and the precipitation of the silver salt, to which they give the formula  $\text{AgCo}(\text{CO})_4 \cdot 1/2\text{CO} \cdot 1/2\text{H}_2\text{O}$ . Further confirmation of the presence of the  $[\text{Co}(\text{CO})_4]^-$  ion they find in the formation of crystalline salts upon the addition of complex cobaltous, nickel, and silver ions, e.g.,



*Behavior with amines.* Hieber and his coworkers have extensively investigated the behavior of the carbonyls with the complex-forming amines. They find in general that, as with nickel carbonyl, the amines displace a part but never all of the carbonyl group of the cobalt carbonyls with the formation of mixed complexes. These new complexes can be isolated as crystalline substances of definite composition, but there is no indication that any of them are volatile. Furthermore, the multiplicity of such complexes is increased through the ability of the cobalt to disproportionate.

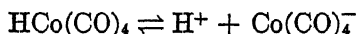
For example, either cobalt tetracarbonyl or cobalt tricarbonyl placed in pyridine causes effervescence (escaping carbon monoxide), and crystalline  $\text{Co}_2(\text{CO})_8\text{py}_4$  finally crystallizes out. In similar fashion such complexes as  $\text{Co}(\text{CO})_3(o\text{-phthr})_2$ ,  $\text{Co}_2(\text{CO})_8 \cdot \text{CH}_3\text{OH}$ , and  $\text{Co}_2(\text{CO})_8 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$  have been isolated. When such complexes are treated with acid there is obtained a small amount of a cobalt compound with a very bad odor. This was the first observation of the cobalt carbonyl hydride (35).

#### *Cobalt carbonyl hydride*

This very volatile substance was first observed by Hieber, Mühlbauer, and Ehman (35); its salts, or the corresponding salts of iron carbonyl hydride, were recognized by Hock and Stuhlman (47), Feigl and Krumholz (12, 13), and Schubert (86), but the cobalt carbonyl hydride was definitely isolated and identified first by Hieber (24). Hieber and Schulten (41) treated cobalt tetracarbonyl with barium hydroxide solution, by means of which the disproportionation outlined in the previous paragraph was effected. Thereafter, treatment with phosphoric acid and vacuum distillation into a trap cooled with liquid air gave the cobalt carbonyl hydride. Hieber and Schulten give its melting point as  $-26.2^\circ\text{C}$ . The light yellow liquid soon turns dark, and at  $-18^\circ\text{C}$ . it effervesces with escape of hydrogen.

Originally Hieber maintained that both the hydride and the metal derivatives of the hydride were non-ionic in nature. In 1937 he admits that the metal derivatives are ionic and that the ion  $\text{Co}(\text{CO})_4^-$  possesses a symmetrical electron shell, but he still contends that the hydride is non-ionic, in fact, he postulates a composite pseudo nickel atom (24),—a coalition of the cobalt and hydrogen atoms, with atomic number 28,—as the center of the complex.

In spite of the instability of cobalt carbonyl hydride in the pure state, it can be carried from one vessel to another as a vapor highly diluted with carbon monoxide at room temperature with practically no decomposition. It dissolves out of such a stream of carbon monoxide in water at 0°C., and although the solution decomposes in a few minutes, it, nevertheless, persists long enough for a rough estimate of its acid strength to be made. Coleman (9) passed carbon monoxide carrying the hydride vapors through a rotary absorption tower containing 200 cc. of distilled water and some methyl orange. The indicator quickly turned red, although somewhat short of the clear red produced by strong acids. Addition of 0.1 *N* potassium hydroxide changed the color to yellow. In all, 3 cc. of 0.1 *N* potassium hydroxide was added, and even in the presence of the salt,  $\text{KCo}(\text{CO})_4$ , absorption of additional hydride caused the methyl orange to turn red. After about ten minutes the red color faded and a little flocculent deposit was noted due to the decomposition of the hydride. Postulating the acid nature,



and making rough estimates of the amount of acid and its neutral salt indicate an ionization constant between that of acetic acid,  $1.8 \times 10^{-5}$ , and that of formic acid,  $2 \times 10^{-4}$ .

It is hard to understand Hieber's point of view, but certainly, according to all ordinary standards, the acid-to-salt relation holds between the cobalt carbonyl hydride and its sodium, potassium, and barium salts. The latter are soluble; although they have not been isolated in the dry condition they must exist in water solution in the ionized condition. It is true, of course, that the mercuric and silver derivatives are insoluble in water and soluble in organic solvents,—benzene, acetone, chloroform, ether,—and, perhaps, complete salt-like nature should not be attributed to them.

#### IRON CARBONYLS

There are three different well-defined iron carbonyls,—the pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , the tetracarbonyl,  $[\text{Fe}(\text{CO})_4]_2$ , and the enneacarbonyl,  $\text{Fe}_3(\text{CO})_9$ . Of these, the pentacarbonyl is the only one which is distinctly volatile, and it is the only one which can be prepared directly from the metal and carbon monoxide.

#### *Preparation of iron pentacarbonyl*

Iron pentacarbonyl is prepared on a large scale by industrial processes (75). It is in general prepared by the action of carbon monoxide upon finely divided iron reduced from the oxide or some other iron compound. High pressure and somewhat elevated temperature (up to 200°C.) work



advantageously. Oxygen and carbon disulfide vapor decrease the activity of the iron. Hydrogen sulfide is reported to be without effect.

In addition to its poisonous effects, iron pentacarbonyl is dangerous on account of the liability of spontaneous combustion. This danger is lessened by the common practice of mixing it with kerosene or other organic solvents.

### *Properties of iron pentacarbonyl*

In contact with air iron pentacarbonyl is oxidized, ferric oxide ( $\text{Fe}_2\text{O}_3$ ) is deposited, and usually carbon monoxide is set free, although under some conditions carbon dioxide is formed. Spontaneous ignition frequently occurs, and the products of burning are ferric oxide and carbon dioxide. When it is shaken with a large amount of distilled water and hydrogen peroxide a deep red transparent ferric oxide sol can be prepared that will remain clear for from two to three months (18, 16).

Halogens do not react as rapidly or as definitely as with nickel carbonyl. The tendency is to form ferrous or ferric halide with liberation of carbon monoxide, but intermediate stages can be identified. At low temperature the addition compounds  $\text{Fe}(\text{CO})_5\text{X}_2$  ( $\text{X}$  = halogen) can be isolated. At room temperature these lose carbon monoxide to leave  $\text{Fe}(\text{CO})_4\text{X}_2$ . With water complete change to the salt-like form of  $\text{FeX}_2$  occurs and all of the carbon monoxide escapes (26, 27).

Dilute acids are without effect. Solutions of hydrogen chloride and hydrogen bromide in chloroform and anhydrous gaseous hydrogen iodide give ferrous halide, carbon monoxide, and free hydrogen (55).

### *Preparation of iron enneacarbonyl*

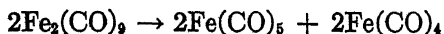
Subjected to the action of sunlight iron pentacarbonyl, either pure or in solvents or in the vapor form, decomposes (89).



The yellow to orange crystals may be washed free of surplus pentacarbonyl with ether. The above reaction is subject to a slow reversal in the dark.

The enneacarbonyl is insoluble in ether, petroleum ether, and benzene, somewhat soluble in alcohol, and more so in pyridine.

Its decomposition begins at about  $80^\circ\text{C}$ . and proceeds according to the following reactions, depending on pressure, solvents, etc.,



The dry crystals of iron enneacarbonyl are very stable in dry air. Moistened with iron pentacarbonyl they quickly lose their luster and frequently ignite spontaneously.

The halogens decompose the enneacarbonyl; for example, bromine water dissolves the crystals and carbon monoxide is liberated. The reactions of the halogens are not as complete as with nickel carbonyl and an intermediate compound,  $\text{Fe}_2(\text{CO})_7\text{Br}_4$ , has been identified (21).

Dilute hydrochloric and sulfuric acids have no action on the enneacarbonyl.

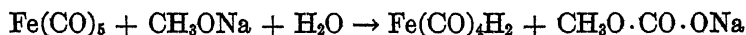
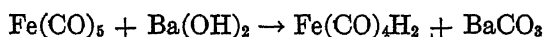
Potassium hydroxide dissolves the enneacarbonyl.

#### *Preparation of iron tetracarbonyl*

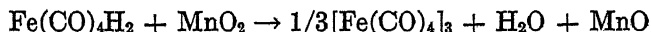
In general, iron tetracarbonyl is a product of the regulated thermal decomposition of iron enneacarbonyl (15, 17, 11). Specifically, if 1 part of the enneacarbonyl and 20 parts of toluene are heated in a sealed, air-free tube to  $95^\circ\text{C}$ . with shaking until the crystals have disappeared, and then the tube is allowed to cool slowly, green crystals of the tetracarbonyl separate out. These crystals may be washed with toluene.

Iron tetracarbonyl is soluble in benzene, petroleum ether, ether, acetone, nickel carbonyl, and iron pentacarbonyl. The solutions are dark green.

A very effective method of preparing iron tetracarbonyl direct from the pentacarbonyl has been devised by Hieber and Leutert (32). The pentacarbonyl is shaken with alkali, barium hydroxide or sodium methoxide, and a suspension of manganese dioxide is added. The pentacarbonyl disproportionates with the formation of the hydride.



The hydride is oxidized:



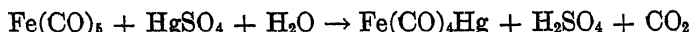
The excess of manganese dioxide is dissolved with ferrous sulfate and sulfuric acid and the iron tetracarbonyl is collected on a filter.

#### *Iron carbonyl hydride, $\text{Fe}(\text{CO})_4\text{H}_2$*

As outlined in the preceding paragraph, treatment of iron pentacarbonyl with alkalis yields iron tetracarbonyl hydride, or its salt. In alkaline solution the hydride is comparatively stable except from attack by oxidizing agents; it is particularly susceptible to air and it can be prepared only in oxygen-free atmospheres. The stability of the hydride in alkalis is quite obviously a consequence of salt formation, although Hieber at first

strongly contested this view. However, when the solution is acidified the free acid is formed. This is extremely unstable and breaks down in a variety of ways, liberating hydrogen and other products. By immediate vacuum distillation of the acidified solution or by sweeping with carbon monoxide the volatile hydride can be transferred to a trap cooled with liquid air and obtained in a pure condition.

The iron tetracarbonyl hydride was first isolated and identified by Hieber and Leutert (30). Previous to that its existence had been surmised. Hock and Stuhlman (47) treated iron pentacarbonyl with mercuric salts,



obtaining the mercury compound as a dark yellow precipitate insoluble in water, acids, acetone, ether, and pyridine. This compound decomposes at 150°C. into carbon monoxide, mercury, and iron. With excess mercuric sulfate the salt  $\text{Fe}(\text{CO})_4\text{Hg} \cdot \text{HgSO}_4$  is obtained; it is somewhat soluble. With mercuric chloride the salt  $\text{Fe}(\text{CO})_4\text{Hg}_2\text{Cl}_2$  is obtained.

Feigl and Krumholz (12) acidified the salts of  $\text{H}_2\text{Fe}(\text{CO})_4$  and, by sweeping with carbon monoxide into a solution of mercuric salt, succeeded in carrying over a volatile compound which again precipitated the same mercury compound. Feigl and Krumholz (13) also prepared  $[\text{Fe}(\text{CO})_4]\text{NaH} \cdot \text{CH}_3\text{OH}$  and the corresponding ethyl alcoholate by treating iron pentacarbonyl with sodium methylate and sodium ethylate in alcohol solution. They believed that the salt-like nature of these compounds, that is, the ionic character of  $\text{Fe}(\text{CO})_4^-$ , was demonstrated by the precipitation with metal ammine solutions of such complexes as  $[\text{Fe}(\text{CO})_4]^-$ ,  $[\text{Cd}(\text{NH}_3)_6]$  and  $[\text{Fe}(\text{CO})_4\text{H}]_2[\text{Fe}(\text{o-phthr})_3]$ .

Coleman (9) found the acid strength of the iron carbonyl hydride much less than that of the cobalt carbonyl hydride. He condensed the vapors in a trap cooled with solid carbon dioxide; after sweeping out all carbon dioxide from the trap he allowed the trap to warm up slowly and then swept the carbonyl hydride vapors into a rotary absorption tower containing indicators. Methyl orange and methyl red were not affected, but phenolphthalein, reddened with a drop of 0.1 *N* potassium hydroxide, was quickly decolorized. In fact, the absorption of the carbonyl hydride could be sharply followed by titration with the 0.1 *N* potassium hydroxide, several cubic centimeters of which were used. The acid strength of iron carbonyl hydride is thus of about the same order of magnitude as that of carbonic acid.

#### *Iron nitrosyl carbonyl*

Mond and Wallis (80) in 1922 showed that a volatile nitrosyl carbonyl was formed by the action of nitric oxide on iron enneacarbonyl, but they were unable to separate it from the pentacarbonyl formed at the same time

and they did not derive its correct formula. Nitric oxide does not react with iron pentacarbonyl alone, and it does not react completely with the enneacarbonyl nor with the tetracarbonyl alone. But Anderson (1) in 1932 used a solution of iron tetracarbonyl in iron pentacarbonyl, allowing nitric oxide to act at 95°C. with a return condenser. The mixture of pentacarbonyl and nitrosyl carbonyl was separated by fractionation at -15°C. At 0°C. the vapor pressures are as follows:  $\text{Fe}(\text{CO})_5$ , 6 mm.;  $\text{Fe}(\text{CO})_2(\text{NO})_2$ , 4.5 mm. At -15°C. the difference is greater. The fractionation was continued until the melting point indicated the purity of the nitrosyl carbonyl.

The iron nitrosyl carbonyl has the formula  $\text{Fe}(\text{CO})_2(\text{NO})_2$ . It consists of dark red crystals melting at 18.5°C. The red liquid easily supercools. It is generally soluble in organic solvents but not in water. Its vapor decomposes considerably at 70°C. and a little even at -15°C. It is quickly oxidized by air and the halogens. Bromine liberates nitric oxide and carbon monoxide completely, but the latter is partly converted to bromphosgene. Iodine in benzene solution liberates carbon monoxide, a small part of which is oxidized to carbon dioxide, and the compound  $\text{Fe}(\text{NO})_2\text{I}_2$  can be isolated. The latter reacts with silver giving silver iodide, and no gas escapes. This may indicate that a polymer  $[\text{Fe}(\text{NO})_2]_n$  is formed. Aqueous hydrogen peroxide and sodium hydroxide liberate carbon monoxide with a considerable amount of carbon dioxide and the nitric oxide is converted to a mixture of sodium nitrite and nitrate.

#### *Non-volatile iron nitrosyls*

Two non-volatile iron nitrosyls which contain no carbonyl groups have been reported. Manchot and Gall (68) shook 10 cc. of iron pentacarbonyl and 50 cc. of anhydrous methyl alcohol at room temperature for twenty-four hours with nitric oxide and obtained a completely black precipitate which seemed to have the formula  $\text{FeNO} \cdot 2\text{CH}_3\text{OH}$ . Manchot and Enk (61) placed about 1 cc. of iron pentacarbonyl in a glass tube and condensed solid nitric oxide by immersing the tube in liquid air. The open tube was placed in a brass autoclave filled with nitric oxide, and the autoclave was slowly warmed to 44-45°C. and kept at that temperature. More rapid heating to higher temperature caused explosive reactions. After some time the autoclave was cooled with carbon dioxide and acetone, and opened; the glass tube was found filled with matted, thread-like, black crystals. These would smoke in the air as they warmed up and nitric oxide would escape, but the crystals themselves appeared to be not volatile. Analysis showed the formula  $\text{Fe}(\text{NO})_4$  and complete absence of carbon monoxide. These crystals reacted strongly with ammonia, pyridine, and hydrazine, but the products were not identified.

$\text{Fe}(\text{NO})_2\text{I}_2$  has been mentioned above.

$\text{Fe}_2(\text{NO})_4\text{I}_3$  has been prepared by Hieber and Bader (27). Nitric oxide does not react with  $\text{Fe}(\text{CO})_4\text{I}_2$  below its decomposition temperature of  $75^\circ\text{C}$ ., but when the latter is held in a current of nitric oxide at  $75\text{--}80^\circ\text{C}$ . it melts and all of the carbon monoxide is expelled quickly together with some iodine; there is left after cooling a black solid of the composition  $\text{Fe}_2(\text{NO})_4\text{I}_3$ . This is barely sublimable in a current of nitrogen. It is unstable in air. With pyridine and dilute acids nitric oxide is rapidly evolved and a ferrous salt is left. Dry heating drives off nitric oxide.

*Mixed ammine complexes of the iron carbonyls*

The number of complex substances derived from iron carbonyls which have been identified is very large. This may be attributed to two reasons: first, the practical one that the reactions of iron carbonyl have been most extensively studied; and second, the theoretical reason that since the electron requirements of the iron atom can not be satisfied in so simple a manner as that of nickel in nickel carbonyl, the number of ways in which this may be accomplished is multiplied.

The following tabulation of mixed carbonyl ammine complexes compiled by Hieber and Becker in 1930 (28) shows the range of 5, 3, 2.5, and 2 moles of carbon monoxide per atom of iron.

$\text{Fe}(\text{CO})_5\text{NH}_3$ $\text{Fe}(\text{CO})_5\text{en}^*$	$\text{Fe}(\text{CO})_3(\text{NH}_3)_2$ $\text{Fe}(\text{CO})_3\text{py}$ $\text{Fe}(\text{CO})_3\text{en}$ $\text{Fe}_4(\text{CO})_{12}\text{en}_3$ $\text{Fe}(\text{CO})_3\cdot\text{CH}_3\text{OH}$	$\text{Fe}_2(\text{CO})_9\text{en}_2$	$\text{Fe}_2(\text{CO})_4\text{py}_3$ $\text{Fe}_2(\text{CO})_4\text{en}_3$
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\* py = pyridine; en = ethylenediamine.

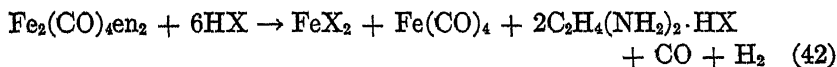
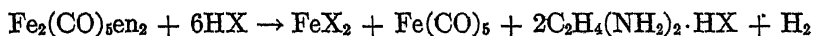
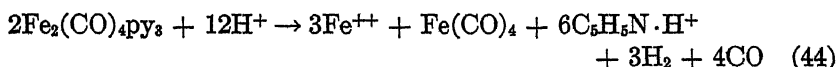
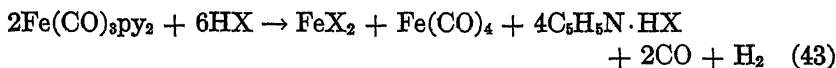
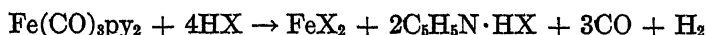
It has already been noted that in the formation of mixed ammine and alcohol neutral complexes of cobalt and nickel, the carbonyl groups are never wholly replaced by the other groups. The same statement holds for iron carbonyls. The only compounds of iron in which the carbonyl groups are entirely replaced by zero valent groups are the nitrosyls  $\text{FeNO}\cdot\text{CH}_3\text{OH}$  and  $\text{Fe}(\text{NO})_4$ , mentioned in the preceding section. It is to be noted that these compounds are not volatile and that their chemical nature is as yet very obscure.

Iron pentacarbonyl does not react directly with anhydrous ammonia, or even with liquid ammonia, and the same is true of the ennea- and tetracarbonyls. In the presence of pyridine, however, the ammonia compound,  $\text{Fe}(\text{CO})_5(\text{NH}_3)_2$ , has been prepared (44).

With pyridine alone, iron pentacarbonyl reacts vigorously, carbon monoxide escaping; at first no definite compounds could be isolated (42), but later, when 5 moles of pyridine were used to 1 mole of iron pentacar-

bonyl, red crystals of  $\text{Fe}(\text{CO})_5\text{py}$  were isolated (43). After a few days a more abundant crop of crystals of  $\text{Fe}(\text{CO})_4\text{py}$  was obtained, and after ten to fourteen days, crystals of  $\text{Fe}(\text{CO})_4\text{py}_2$ . Removal of the carbon monoxide was necessary to obtain the last-named product; in other words the replacement of carbon monoxide by pyridine is a reversible reaction. These mixed complexes are formed as crystalline compounds only under very special conditions,—often very low temperature, and always absence of air and moisture. When isolated, such complexes show no sign of being volatile without decomposition, but they are always of little stability. The pyridine complexes just mentioned are pyrophoric. A further pyridine complex of the formula  $\text{Fe}_2(\text{CO})_4\text{py}_3$  was isolated (44) and when iodine also was present a substance of the formula  $\text{Fe}(\text{CO})_5\text{py}_2\text{I}_2$  could be separated; the latter on standing in pyridine finally gave  $\text{FeI}_2 \cdot 6\text{C}_5\text{H}_5\text{N}$ . The last is either a completely polar compound or it needs only an ionizing solvent to make it so.

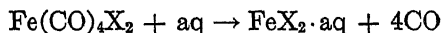
The straight carbonyls are without action with dilute non-oxidizing acids. The substituted carbonyls, particularly where the substituents are basic amines, react readily with acids. In such cases the amines are removed as the hydrochlorides, the CO groups are reapportioned, and ferrous ions are produced at the expense of hydrogen liberated. A few examples of such behavior are shown by the following equations:



#### *Mixed halogen carbonyl complexes*

In the absence of water and of solvents which may form solvates, the halogens seem to be able to play somewhat the same rôle in complex building as do the carbonyl, nitrosyl, and amine groups. For example, dry halogen and dry iron pentacarbonyl yield  $\text{Fe}(\text{CO})_4\text{X}_2$  with liberation of one CO (26). Excess of halogen fails to displace more than one CO. These complexes are shown to be monomolecular by the freezing-point method in indifferent solvents (27, 36).  $\text{Fe}(\text{CO})_4\text{Cl}_2$  is pure yellow. It decomposes at  $10^\circ\text{C}$ . into  $\text{FeCl}_2$  and  $4\text{CO}$ . The corresponding bromide,

$\text{Fe}(\text{CO})_4\text{Br}_2$ , is darker colored and decomposes at  $55^\circ\text{C}$ .  $\text{Fe}(\text{CO})_4\text{I}_2$  is deep brown and decomposes at  $75^\circ\text{C}$ . These halogen complexes cannot be prepared from the simple iron halides and carbon monoxide. The complexes decompose with water,



instantly in the case of the chloride, slowly in the case of the iodide. Similar decompositions take place with ammonia, amines, alcohols, esters, ketones, and aldehydes. On the other hand, all three of these carbonyl halides are stable in glacial acetic acid.

Just as addition products of iron pentacarbonyl with amines, e.g.,  $\text{Fe}(\text{CO})_5\text{en}$  (43) can be isolated, prior to the escape of carbon monoxide, so in similar manner addition products with the halogens have been isolated without escape of carbon monoxide. Equimolal amounts of  $\text{Fe}(\text{CO})_5$  and of halogen in ether or petroleum ether at  $-80^\circ\text{C}$ . give a precipitate of  $\text{Fe}(\text{CO})_5\text{X}_2$ . The chloride is yellow, the bromide is a darker yellow, and

TABLE 7  
*Mixed carbonyl halides*

$\text{Fe}(\text{CO})_5\text{X}_2^*$	$\text{Fe}(\text{CO})_4\text{X}_2$ $\text{Fe}(\text{CO})_4\text{en}_2\text{I}_2$	$\text{Fe}(\text{CO})_3\text{Hg}_2\text{I}_2$	$\text{Fe}(\text{CO})_2\text{py}_2\text{I}_2$ $\text{Fe}(\text{CO})_2(o\text{-phen})_2\text{I}_2$ $\text{Fe}(\text{CO})_2(o\text{-phthr})_2\text{I}_2$ $\text{Fe}(\text{CO})_2(\text{CN})_2\text{py}$	$\text{Fe}(\text{CO})\text{py}_2\text{I}_2$  $[\text{Fe}(\text{CN})_2(\text{CO})]\text{K}$
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\* X = Cl, Br, or I; *o*-phen = *o*-phenylenediamine; *o*-phthr = *o*-phenanthroline.

the iodide is a deep brown-red solution. The chloride decomposes at  $-35^\circ\text{C}$ . into  $\text{Fe}(\text{CO})_4\text{Cl}_2$  and carbon monoxide; the bromide decomposes at  $-10^\circ\text{C}$ ., and the iodide only at  $0^\circ\text{C}$ .

A particularly stable substance is obtained (27) by treating diiron tetracarbonyl tripyridine with cyanogen



The substance is stable up to  $100^\circ\text{C}$ . and is not decomposed by potassium cyanide, acids, or pyridine.

Hieber and Bader give an interesting table (table 7) of the mixed carbonyl halides, showing a complete range from one to five carbonyl groups for each iron atom.

#### REACTIONS OF NITROSYL CARBONYLS WITH AMINES

The nitrosyl carbonyls show much the same kind of behavior with amines as do the straight carbonyls, but it is noteworthy that in such reaction

only the carbonyl group is displaced. For example, Hieber (25) reports the formation of the following complexes:  $\text{Fe}_2(\text{NO})_4\text{py}_3$ ;  $\text{Fe}(\text{NO})_2(o\text{-phthr})$ ;  $\text{Co}_2(\text{NO})_2\text{COp}_2$ ;  $\text{CoNO}(\text{CO})_2(o\text{-phthr})$ ;  $\text{CoNOCO}(o\text{-phthr})$ . The halogens on the other hand, as already mentioned, displace both carbon monoxide and nitric oxide with the formation of cobaltous and ferrous halides. Chlorine and bromine do so without the formation of intermediate products, while iodine in benzene solution displaces the carbon monoxide and the intermediate product  $\text{Fe}(\text{NO})_2\text{I}_2$  can be separated.

Anderson and Hieber find in the easier displacement of carbon monoxide evidence for a different electronic binding of carbon monoxide and nitric oxide to the central atom. For carbon monoxide they find the bonding to be of the "coördinative covalence" type (i.e.,  $\text{M}:\text{C}::\text{O}:$ , as designated earlier in this paper under formula I, p. 9), whereas for nitric oxide they hold that the bonding is a composite of the coördinative covalence and pure covalence types ( $\text{M}::\text{N}::\text{O}:$ , as shown in formula II).

Although it is recognized that either type I or type II is a possible method of bonding for either carbon monoxide or nitric oxide, it hardly seems probable that replacement of CO by NO in a series of complexes of such very similar properties as  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}(\text{NO})(\text{CO})_3$ , and  $\text{Fe}(\text{NO})_2(\text{CO})_2$  should be accompanied by a change of the electron symmetry of the central atom. It is far simpler to attribute the greater tenacity of the nitric oxide bonding to the different distribution of the positive kernel charges.

#### RUTHENIUM CARBONYLS

It had been known for some time that metals of the platinum family as well as copper, silver, gold, and mercury could form mixed carbonyl compounds, many of them capable of being sublimed. In fact, Mond had prepared a straight carbonyl of ruthenium (76, 80) by heating ruthenium sponge in carbon monoxide under a pressure of 400 atmospheres at  $300^\circ\text{C}$ . He obtained a yellow-orange precipitate and a metal mirror in the tube. The yellow compound was insoluble in hydrochloric acid but dissolved in nitric acid and bromine water with evolution of carbon monoxide. Its composition approximated the formula  $\text{Ru}(\text{CO})_2$ .

It remained, however, for Manchot and Manchot (73) in 1936 to show that ruthenium can form a very volatile carbonyl,—in fact, a series of carbonyls closely resembling iron pentacarbonyl, iron enneacarbonyl, and iron tetracarbonyl, the pentacarbonyl being the volatile member of the series with ruthenium as well as with iron. The volatile ruthenium carbonyl stands in the same relation to the inert gas xenon that iron pentacarbonyl does to krypton.

The pentacarbonyl was first prepared by these men from ruthenium



sponge and carbon monoxide at 700 atmospheres and 400°C. The high pressure was produced by condensing the carbon monoxide with liquid nitrogen in a brass vessel connected with the autoclave containing the ruthenium sponge. Accumulation of the pentacarbonyl in the ruthenium sponge soon inhibited the reaction, but occasional opening of the exit valve allowed this to be swept out and its formation in the autoclave to proceed. The vapors of the ruthenium pentacarbonyl were condensed at low temperature from the carbon monoxide stream. A more effective method of preparing the pentacarbonyl was soon devised: A mixture of 1 g. of ruthenium triiodide and 5 g. of finely divided silver subjected in an autoclave to carbon monoxide under 455 atmospheres at 170°C. gave in twenty-four hours a large yield of the pentacarbonyl.

Ruthenium pentacarbonyl condenses to colorless crystals which melt at  $-22^{\circ}\text{C}$ . to a colorless liquid of high vapor pressure. The liquid decomposes slowly above its melting point into the enneacarbonyl,  $\text{Ru}_2(\text{CO})_9$ . However, by working rapidly in a vacuum the liquid may be completely vaporized to a colorless gas, which can again be condensed at  $-23^{\circ}\text{C}$ . to colorless crystals or supercooled liquid.

Ruthenium pentacarbonyl is soluble in benzene, alcohol, etc., but it is unstable in these solvents. Like iron pentacarbonyl it decomposes in the light. Ruthenium pentacarbonyl vapors passed into a concentrated (1:1) potassium hydroxide solution give a brown-red solution of strong reducing properties.

From the breakdown of the pentacarbonyl the enneacarbonyl is obtained. This is an orange colored substance. It is quite stable against air and light, and it can be sublimed. Its decomposition yields a green substance which is probably the polymer of the tetracarbonyl, although a reliable analysis has not been achieved.

From the enneacarbonyl and iodine the mixed carbonyl halide,  $\text{Ru}(\text{CO})_2\text{I}_2$ , is obtained. The latter, warmed with silver in a current of carbon monoxide, gives the pentacarbonyl.

This carbonyl halide had been prepared in 1924 by Manchot and König (69) by heating ruthenium triiodide in a current of carbon monoxide at atmospheric pressure at  $250^{\circ}\text{C}$ . The residue,  $\text{Ru}(\text{CO})_2\text{I}_2$ , is an ochre-colored powder, very unreactive toward hydrochloric and concentrated sulfuric acids and insoluble in organic solvents. Similar compounds,  $\text{Ru}(\text{CO})_2\text{Br}_2$  and  $\text{Ru}(\text{CO})_2\text{Cl}_2$ , were prepared. These can be sublimed. The enneacarbonyl, heated to  $190^{\circ}\text{C}$ . under high pressure in nitric oxide, yields a red nitrosyl, free from carbon monoxide; the uncertain analysis indicates its formula as  $\text{Ru}(\text{NO})_4$  or  $\text{Ru}(\text{NO})_5$ , and it would seem to correspond to the non-volatile iron nitrosyl  $\text{Fe}(\text{NO})_4$ .

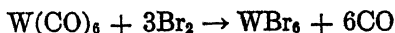
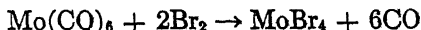
## CARBONYLS OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

A volatile carbonyl of molybdenum was prepared as early as 1910 by Mond (76) by direct synthesis at high pressure and temperature. The amount obtained was small and the analysis, giving the formula  $\text{Mo}_3(\text{CO})_{26}$ , was uncertain. The pressure method for obtaining molybdenum and tungsten carbonyls,  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$ , in larger amounts was improved and patents were taken out by the I. G. Farbenindustrie A.-G. (49) in 1931. Chromium, however, utterly fails to yield the carbonyl in this manner.

Meanwhile, Job and Cassal (51) had applied to the problem the discoveries of Job and Reich regarding the behavior of carbon monoxide and the Grignard reagent in the presence of metal salts. Carbon monoxide is absorbed with reasonable rapidity about in proportion to the Grignard reagent used when a little chromic chloride is present. Upon hydrolysis of the Grignard mixture an amount of chromium hexacarbonyl small in proportion to the carbon monoxide used is recovered. Small as the yield is, the substance is obtained in great purity and in amount sufficient for its identification and a study of its properties. Later the same method was employed with molybdenum pentachloride and tungsten hexachloride for the preparation of the hexacarbonyls of molybdenum and tungsten, respectively.

Chromium hexacarbonyl was prepared in 1934 by this method by Windsor and Blanchard (92), who confirmed the formula  $\text{Cr}(\text{CO})_6$  by analysis and vapor density measurements. The vapor pressure ranges from 0.04 mm. at  $0^\circ\text{C}$ . to 66.5 mm. at  $100^\circ\text{C}$ . At  $100^\circ\text{C}$ . slow decomposition takes place and interferes with the vapor pressure determination.

Hieber and Romberg (37) in 1935 prepared the hexacarbonyls of chromium, molybdenum, and tungsten by the Grignard method. All three form beautiful, colorless, strongly refracting crystals. The hexacarbonyls are remarkably stable in comparison with the other carbonyls, the vapors decomposing noticeably only at about  $120^\circ\text{C}$ . and thereby depositing a very pure metallic mirror. At ordinary temperature concentrated hydrochloric and sulfuric acids are without effect; chromium carbonyl is in fact stable toward bromine and iodine. Concentrated nitric acid oxidizes the hexacarbonyl rapidly. With alkalis there is no formation of carbonate or of carbonyl hydride; in this respect the behavior is the same as that of nickel carbonyl. The reaction with halogens does not give carbonyl halides, but the displacement of carbon monoxide is quantitative.

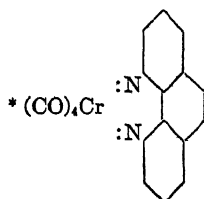


The volatility of the hexacarbonyls decreases slightly in the order chromium, molybdenum, tungsten. Extrapolating from the vapor pressure curves Hieber and Romberg (38) obtained the following boiling points:  $\text{Cr}(\text{CO})_6$ ,  $420.5^\circ\text{A}$ .;  $\text{Mo}(\text{CO})_6$ ,  $429.4^\circ\text{A}$ .;  $\text{W}(\text{CO})_6$ ,  $448.0^\circ\text{A}$ .

### *Amine-substituted carbonyls*

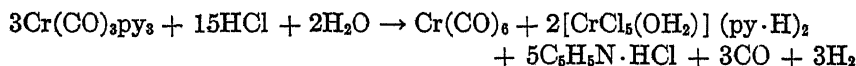
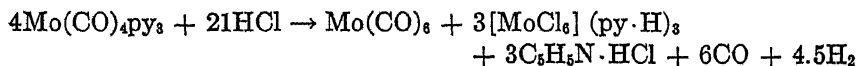
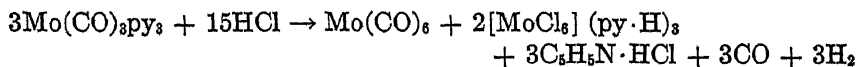
The greater stability of these hexacarbonyls as compared with the carbonyls of nickel, cobalt, and iron is also reflected in the greater difficulty with which amine substitutions are effected (34, 39). Hieber and Mühlbauer and Hieber and Romberg have succeeded in isolating the following compounds:

$\text{Cr}(\text{CO})_4\text{py}_2$	$\text{Mo}(\text{CO})_3\text{py}_3$	$\text{W}(\text{CO})_3\text{py}_3$
$\text{Cr}_2(\text{CO})_7\text{py}_3$	$\text{Mo}(\text{CO})_3\text{py}_2$	$\text{W}(\text{CO})_4\text{py}_2$
$\text{Cr}(\text{CO})_3\text{py}_3$	$\text{Mo}(\text{CO})_4(o\text{-phthr})$	$\text{W}(\text{CO})_4(o\text{-phthr})$
$\text{Cr}(\text{CO})_4(o\text{-phthr})^*$	$\text{Mo}(\text{CO})_3\text{py}(o\text{-phthr})$	$\text{W}(\text{CO})_3\text{py}(o\text{-phthr})$
$\text{Cr}_2(\text{CO})_6\text{py}_3$	$\text{Mo}_2(\text{CO})_6\text{en}_3$	



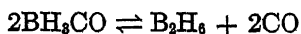
The behavior of these amine-substituted carbonyls with acids is very similar to that of the corresponding compounds of nickel, cobalt, and iron; the carbonyl groups are reappportioned with the formation of hexacarbonyl and escape of carbon monoxide, and metal ions and a corresponding amount of free hydrogen are formed.

The following equations are given as typical (34):

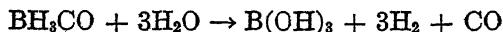


### BORINE CARBONYL

Burg and Schlesinger (8) have very recently shown the existence of a compound of the formula  $\text{BH}_3\text{CO}$ . This substance can exist in gaseous mixture in equilibrium with diborane and carbon monoxide,



an idea of its stability being given by the statement that a sample of pure  $\text{BH}_3\text{CO}$  at an initial pressure of 200 mm at  $100^\circ\text{C}$ . would be 95 per cent decomposed when equilibrium was reached (neglecting minor side reactions in which a little hydrogen and some less volatile products are produced). It is best prepared by heating a mixture of carbon monoxide and diborane at  $90^\circ\text{C}$ . for 15 min.; under these conditions the gaseous equilibrium mentioned above is practically attained. The borine carbonyl may be isolated by condensation at low temperatures. At  $-111.8^\circ\text{C}$ . its vapor pressure is 25.4 mm. Its melting point is estimated at  $-137^\circ\text{C}$ ., and its boiling point at  $-64^\circ\text{C}$ . It hydrolyzes according to the equation



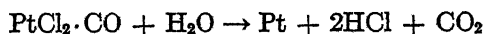
the reaction being quantitative after three hours at  $100^\circ\text{C}$ . From the volume changes during formation and decomposition this substance is shown to be monomolecular according to the formula  $\text{BH}_3\text{CO}$ .

The above authors were interested in the study of this compound as a means of indicating the transitory existence of monomolecular borine,  $\text{BH}_3$ . The electron arrangement of the ordinary diborane,  $\text{B}_2\text{H}_6$ , is still a puzzle. For the borine carbonyl they favor the structure in which "borine and carbon monoxide are joined by a coördinate link consisting of electrons furnished by the carbon monoxide". This would correspond to the carbonyl linkage I (see p. 9) as follows:  $\text{H}_3\text{B}:\text{C}:::\text{O}:$  and boron would have the effective atomic number of 10. Carbonyl linkage II would not fit this compound.

It is very evident that borine carbonyl has the distinguishing characteristics of the volatile metal carbonyls and should be included in that classification.

#### CARBONYL HALIDES OF THE NOBLE METALS

*Platinum* compounds with carbon monoxide were first prepared in 1868 by Schützenberger (87), who passed chlorine and carbon monoxide over platinum sponge at  $250^\circ\text{C}$ . and obtained a yellow sublimate (or liquid which crystallized on cooling). This sublimate dissolved in carbon tetrachloride and three distinct compounds were isolated:  $\text{PtCl}_2 \cdot \text{CO}$ ,  $\text{PtCl}_2 \cdot 2\text{CO}$ , and  $2\text{PtCl}_2 \cdot 3\text{CO}$ . These compounds are convertible into one another under the right conditions. They dissolve unchanged in carbon tetrachloride but are decomposed with water:



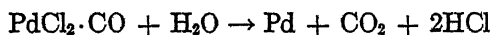
The other two carbonyl halides give the same products and the surplus carbon monoxide escapes. Schützenberger's experiments were confirmed much later by others, especially Mylius and Foerster (81) and Manchot (59). By treating a carbon tetrachloride solution of the platinum com-

pounds with ammonia the compounds  $\text{PtCl}_2 \cdot \text{CO} \cdot 2\text{NH}_3$  and  $\text{PtCl}_2 \cdot 2\text{CO} \cdot 2\text{NH}_3$  were isolated; with ethylene the compound  $\text{PtCl} \cdot \text{CO} \cdot \text{C}_2\text{H}_4$  was isolated. Manchot made use of the volatility of the platinum chloride carbonyls as a practical method of separating platinum from palladium.

*Iridium.* Manchot and Gall prepared a similar sublimable carbonyl chloride of iridium (64). Dry iridium trichloride in a current of completely dry carbon monoxide at  $150^\circ\text{C}$ . yields a white, sublimable, crystalline substance of the composition  $\text{Ir}(\text{CO})_2\text{Cl}_2$ . This decomposes in water with the evolution of carbon monoxide.

*Osmium.* Manchot and König (70) heated osmium trichloride in a stream of carbon monoxide at 1 atmosphere at  $270^\circ\text{C}$ . and obtained a white sublimate whose composition approximated the formula  $\text{OsCl}_2 \cdot 3\text{CO}$ . This compound is indifferent to water and acids. It dissolves in sodium hydroxide solution; after neutralization with nitric acid all of the chlorine is precipitated by silver nitrate, leaving the osmium and carbon monoxide in solution as an apparently stable complex.

*Palladium* forms the least stable halogen carbonyl complex of all of the platinum metals. Complexes of the others can be sublimed away leaving only the palladium untouched. At low temperature, however, Manchot and König (72) succeeded in isolating a compound of the composition  $\text{PdCl}_2 \cdot \text{CO}$ . Strangely enough, the presence of alcohol favored the formation of this compound. Dry carbon monoxide saturated with the vapor of methyl alcohol was passed over dry  $\text{PdCl}_2$  at  $0^\circ\text{C}$ . and the latter was converted to the light yellow-brown complex. The latter is decomposed by water.



*Rhodium* differs from the other platinum metals in that no simple carbonyl halide has been discovered, but the compound  $\text{RhCl}_2 \cdot \text{RhO} \cdot 3\text{CO}$ , prepared by Manchot and König (71), excels all of the carbonyl halides of this series in volatility. No results were obtained by heating anhydrous rhodium trichloride in carbon monoxide even to high temperatures, but when carbon monoxide was passed over moist rhodium trichloride a change began at  $50^\circ\text{C}$ . At  $140^\circ\text{C}$ . beautiful, ruby-red, needle-like crystals sublimed, sometimes 3 cm. in length. At  $300^\circ\text{C}$ . decomposition of the substance takes place with the deposit of a metallic mirror. Analysis gives the formula as shown above, and the molecular weight by the freezing-point method in benzene corresponds closely to that formula. The substance dissolves with difficulty in cold water, but more rapidly in warm water with an orange-red color. On further warming or after a long time in the cold the solution grows cloudy and metallic rhodium deposits. At  $125.5^\circ\text{C}$ . the substance melts to a brown liquid; meanwhile a part vaporizes

with a strong blue fluorescence. It is somewhat volatile at ordinary temperature, because on standing the walls of the vessel become dark. It is soluble in carbon tetrachloride, benzene, and glacial acetic acid.

*Ruthenium* trihalides react with carbon monoxide according to the equation



At 250°C. and 1 atmosphere the black triiodide reacts completely in 30 min., an ochre-colored residue remaining and iodine vapors escaping. This residue of  $\text{Ru}(\text{CO})_2\text{I}_2$  is insoluble in water and in organic solvents. It is very resistant to concentrated hydrochloric acid and concentrated sulfuric acid (69).

The similar reaction with ruthenium tribromide is very much slower, but, unlike the carbonyl iodide, the product,  $\text{Ru}(\text{CO})_2\text{Br}_2$ , sublimes and is obtained distinct from the unaffected residue. At very high carbon monoxide pressure at 185–188°C. there is a further reduction of the bromide to  $\text{RuCOBr}$  (62). This new carbonyl bromide is a colorless crystalline substance. Heated to 200°C. in an indifferent gas it disproportionates into  $\text{Ru}(\text{CO})_2\text{Br}_2$ , which sublimes, and ruthenium.

The ruthenium trichloride reacts with carbon monoxide much more slowly than the iodide or the bromide. The product is the same,  $\text{Ru}(\text{CO})_2\text{Cl}_2$ , and it sublimes away from the unaffected residue even more easily than the carbonyl bromide. High pressure of carbon monoxide fails to produce a compound similar to  $\text{RuCOBr}$ , but it does give a very small quantity of a halogen-free product which appears to be identical with the non-volatile carbonyl of Mond. This halogen-free carbonyl is also produced in small amounts from the iodide.

*Copper.* The familiar use of either acidic or ammoniacal solutions of cuprous chloride as an absorbent for carbon monoxide in gas analysis rests on the formation of a copper carbonyl halide. Manchot and Friend (63) found the upper limit of the absorption ratio  $\text{CO}:\text{CuCl}$  to be 1:1. At 0°C. they succeeded in obtaining colorless crystals of the composition  $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$  independent of whether the solution were acid, neutral, or weakly ammoniacal. These crystals immediately began to give off carbon monoxide when taken out of the atmosphere of that gas.

*Silver.* The absorption of carbon monoxide by silver salt under very unusual conditions has been observed by Manchot (60). Aqueous silver salt solutions have no action with carbon monoxide, but sulfuric acid solutions do absorb the gas, in fact, the more concentrated the solution, even up to fuming acid of 50 per cent  $\text{SO}_3$  content, the greater the absorption. It is evident that the effect of the sulfuric acid is due to its dehydrating action, because similar effects are obtained by adding phosphoric

anhydride to the dilute solutions. The maximum absorption ratio is  $1\text{CO}$  to  $1\text{Ag}_2\text{SO}_4$ , and the formula of the complex is deduced as  $\text{Ag}_2\text{SO}_4 \cdot \text{CO}$ .

*Gold.* Anhydrous gold trichloride, subjected to the action of dry carbon monoxide, begins to show a sublimate at  $55^\circ\text{C}$ . At higher temperatures the reaction is more rapid, but reduction to metallic gold complicates the process. The best procedure (65) proved to be to pass dry carbon monoxide mixed with 10 per cent of dry chlorine over dry gold trichloride at  $115\text{--}120^\circ\text{C}$ .

A similar sublimate was obtained with  $\text{AuCl}$  and carbon monoxide (without the chlorine). The sublimate consisted of beautiful, lustrous, colorless, very transparent crystals several millimeters in length. The substance is extraordinarily sensitive to water, even to the moisture of the air. The ratio  $\text{Au}:\text{Cl}:\text{CO}$  in the substance was shown to be  $1:1:1$ , which indicates the composition  $\text{AuCl} \cdot \text{CO}$ .

*Mercury.* Alcoholic mercuric acetate absorbs carbon monoxide freely, but there is controversy over the nature of the product. Schoeller, Schrauth, and Essers (85) regard it as a mercury-substituted ester of formic acid,  $\text{CH}_3\text{COOHg} \cdot \text{CO} \cdot \text{OR}$ ; Manchot (58) regards it as a carbonyl with the characteristic metal-carbonyl bond,  $\text{CO} \cdot \text{Hg}(\text{OC}_2\text{H}_5)(\text{COOCH}_3)$ .

#### DISCUSSION

It is very difficult to appraise the significance of the volatility of the carbonyl halides of the platinum metals. It is quite clear that the volatility is of a lower order of magnitude than that of the carbonyls that have been listed as volatile. Even chromium carbonyl (vapor pressure 0.26 mm. at  $20^\circ\text{C}$ .) has probably a much higher vapor pressure than the most volatile of the carbonyl halides,  $\text{RuCl}_2 \cdot \text{RhO} \cdot 3\text{CO}$ , which is the only one to show evidence of vaporization at room temperature. No vapor density determinations of the carbonyl halides have been made, and there is no certainty that dissociation does not take place during the process of sublimation (as with ammonium chloride). It would seem nearly certain that the carbonyl linkage to the metal atom is the same as in the volatile carbonyls, because even although the breakup of the complex often gives carbon dioxide, owing to the oxidation of the carbonyl group, there is clear evidence of the dissociability of the carbonyl linkage in this series of compounds.

The great range of the stability of the carbonyls is remarkable,—from those which can exist only at temperatures well below  $0^\circ\text{C}$ . to those, like  $\text{Ru}(\text{CO})_2\text{I}_2$ , which withstand fairly high temperatures and strong chemicals. There is apparently little relationship between the structural forms which produce volatility and those which produce stability of the carbonyl linkage. There is no apparent relationship among the carbonyl

halides between the progressive atomic numbers of the central atoms and the number of carbonyl groups, or the substitution of nitrosyl for carbonyl groups as in the series  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}(\text{CO})_2\text{NO}$ , and  $\text{Fe}(\text{CO})_2(\text{NO})_2$ . There is, in fact, no evidence of a tendency among the carbonyl halides for the central atom to acquire the effective atomic number of an inert gas.

The study of the carbonyls seems to establish the principle that the effective atomic number of the central atom of a complex has an important influence on the field of the complex. This field will be self-contained and the complex be volatile only when the effective atomic number is equal to that of an inert gas. Obviously the effective atomic number of the central atom is not of itself enough to establish a self-contained field over the whole complex. The symmetry of the structure and the charges of the surrounding groups must coördinate with that of the central atom.

TABLE 8

*Volatile carbonyls already known (in Roman type) or to be sought (in italics)*

$\text{Ni}(\text{CO})_4$	$\text{Pd}(\text{CO})_4$	$\text{Pt}(\text{CO})_4$
$\text{Fe}(\text{CO})_5$	$\text{Ru}(\text{CO})_5$	$\text{Os}(\text{CO})_6$
$\text{Cr}(\text{CO})_6$	$\text{Mo}(\text{CO})_6$	$\text{W}(\text{CO})_6$
$\text{CoNO}(\text{CO})_3$	$\text{RhNO}(\text{CO})_3$	$\text{IrNO}(\text{CO})_3$
$\text{Co}(\text{CO})_4\text{H}$	$\text{Rh}(\text{CO})_4\text{H}$	$\text{Ir}(\text{CO})_4\text{H}$
$\text{Fe}(\text{NO})_2(\text{CO})_2$	$\text{Ru}(\text{NO})_2(\text{CO})_2$	$\text{Os}(\text{NO})_2(\text{CO})_2$
$\text{Fe}(\text{CO})_4\text{H}_2$	$\text{Ru}(\text{CO})_4\text{H}_2$	$\text{Os}(\text{CO})_4\text{H}_2$
$\text{Ni}(\text{CO})_4$	$\text{CoNO}(\text{CO})_3$	$\text{Fe}(\text{NO})_2(\text{CO})_2$
$\text{Ni}(\text{CO})_4$	$\text{Co}(\text{CO})_4\text{H}$	$\text{Fe}(\text{CO})_4\text{H}_2$
		$\text{Mn}(\text{NO})_3\text{CO}$
		$\text{Mn}(\text{CO})_4\text{H}_2$
		$\text{Cr}(\text{NO})_4$
		$\text{Cr}(\text{CO})_4\text{H}_4$

The influence of the effective atomic number of the central atom in complex ions can be compared with its influence in the electrically neutral carbonyl complexes. When the complex is charged it cannot escape from the electrostatic influence of the oppositely charged ions and volatility is not to be expected. On the other hand, the ionic condition itself is dependent on the uniformity of the electrostatic field of the whole ion. The net charge not being segregated in any one spot in the ion lessens its chance of degenerating into a non-polar chemical bond. It is naturally far more difficult to trace the connection between effective atomic numbers and the formation of complex ions, because of the greater uncertainties of the latter problem. For example, the degree of solvation of the ion is difficult to estimate, but it does affect the effective atomic number of the central atom.

The effective atomic number concept serves so well in systematizing the very volatile carbonyls that are already known, that we may well conclude this review by making a list of the additional volatile compounds which the concept would lead us to expect. The stability of such substances may be

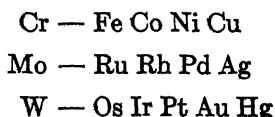


very low, but, according to the concept, if the molecule would hold together at all it would have little external field and the substance would be volatile. The recent success of Manchot in preparing the very volatile ruthenium pentacarbonyl gives some ground for hoping that some other members of the series may be experimentally verified. In table 8 the as yet undiscovered members of the several series (horizontal lines) are printed in italics.

In addition to the compounds listed in table 8, there might be added, with a question mark,  $\text{Ni}(\text{NO})_2\text{CO}$  and  $\text{Co}(\text{NO})_3$ . The effective atomic number concept would allow of such compounds if the arrangement of three groups around the central atom could allow a self-contained field. It is recalled that no such compound of nickel has been discovered, although many experiments, particularly those of Frazer and Trout (14), have been made in which the formation of such a compound might have been noted. A cobalt nitrosyl,  $\text{Co}(\text{NO})_3$ , is mentioned by Hieber (24) with the implication that it is also a volatile compound, but no authoritative description of its formation or of its properties has as yet appeared.

It is noteworthy that no carbonyl compound whatever of manganese has been prepared.

Omitting manganese, mazarium, and rhenium, the metals with which the peculiar dissociable carbonyl linkage occurs occupy a solid block of the periodic arrangement:



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# THE CHELATE RINGS

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The term "chelate," proposed by Morgan (179) to designate those cyclic structures which arise from the union of metallic atoms with organic and inorganic molecules, is derived from the Greek word *chela*, referring to the great claw of the lobster and other crustaceans, and is applicable to these ring systems because of the caliper-like character of the associating molecule.

The formation of these rings may involve either primary or secondary valence. In subsequent papers Morgan used the expression "chelate rings" to cover all three types, that is, rings formed by two primary valences, by one primary and one secondary valence, or by two secondary valences.

With the discovery of compounds in which the metal atom was linked to the organic molecule through three and even four groups Morgan devised for these compounds the names "tridentate," literally, three-toothed, and "quadridentate," four-toothed.

Because of the little attention which this field has attracted, the simple variation of acidic and coördinating groups in the polydentate molecules has escaped investigation. The following classification is, however, obvious:

A. Unidentate

1. Either acidic or coördinating (groups held in the coördination sphere)

B. Bidentate

1. Two acidic groups ( $\text{SO}_4^{--}$ ,  $\text{C}_2\text{O}_4^{--}$ , etc.)
2. One acidic group, one coördinating group ( $\beta$ -diketones, amino acids, dioximes, etc.)
3. Two coördinating groups (ethylenediamine, dipyridyl, etc.)

C. Tridentate

1. Three acidic groups
2. Two acidic groups, one coördinating group

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3. One acidic group, two coördinating groups
4. Three coördinating groups
- D. Quadridentate
  1. Four acidic groups
  2. Three acidic groups, one coördinating group
  3. Two acidic groups, two coördinating groups
  4. One acidic group, three coördinating groups
  5. Four coördinating groups

and so on for quinquidentate and sexadentate.

Of class A thousands of members are known; of classes B1, B2, and B3 numerous examples exist; of class C4 a few examples are known; but of classes C1, C2, and C3 the knowledge is very scanty. Among quadridentate compounds members of classes D3 and D5 only are known. No quinquidentate or sexadentate compounds have been recorded knowingly.

#### CHARACTER OF COMPLEXES FORMED

Among all the classes the valence of the complex radical is equal to the valence of the central metal atom minus the number of primary valence groups<sup>2</sup> held in the coördination sphere. The successive replacement of simple coördinating groups in the coördination sphere by acidic groups leads to series of compounds the complex ions of which have successively changing ionic charges. The metals of coördination number four furnish series of five compounds; those of coördination number six, seven compounds.

The non-electrolyte members of these series are of particular interest. Among the ordinary coördination compounds (unidentate series) the non-electrolytes have practically zero equivalent conductance but are generally soluble in water. The non-electrolytes which are chelate in character (occur in the polydentate series), however, have very unusual properties and were designated by Ley (134) as *inner complex* compounds. They are extremely insoluble in water but usually soluble in non-polar solvents.<sup>3</sup> They usually have very striking colors widely different from the colors of the normal salts of the metals. They generally possess exceptional stability. The term "inner complex" is frequently confused with

<sup>2</sup> Primary or principal valence here is differentiated from secondary or coördinating valence in that the formation of the valence link in the former case involves the replacement of a hydrogen atom, while in the latter case no such replacement occurs. No implication is intended that a difference in the bonds exists once they are formed. In formulating the complex compounds a primary valence will be indicated by a full line and a secondary valence by a dotted line, but this distinction is only for the purpose of keeping track of the valences.

<sup>3</sup> As exceptions to this rule are the derivatives of the simple  $\alpha$ -amino acids, which frequently crystallize with water of crystallization and are somewhat soluble.

the term "chelate" in the older literature. As the unusual properties ascribed to the inner complexes are not characteristic of all chelate compounds but only of those which are at the same time non-electrolytes, the term "inner complex" must be reserved specifically for chelate non-electrolytes.

In addition, the ring formation of various chelating organic molecules is often limited to certain specific metals. This specificity, combined with the properties just mentioned, makes the inner complexes ideal for the purposes of analytical chemistry.

Excluding for the time those mixed compounds which contain both unidentate and bidentate groups associated with the metal atom, the types of compounds derived from metals of various valences with bidentate groups are as follows:

*Coördination number six*

P.V.* = 2	P.V. = 3	P.V. = 4	P.V. = 5
$[M(B1)_3]^{-4}$	$[M(B1)_3]^{-3}$	$[M(B1)_3]^{-2}$	$[M(B1)_3]^{-1}$
$[M(B2)_3]^{-1}$	$[M(B2)_3]^0$	$[M(B2)_3]^{+1}$	$[M(B2)_3]^{+2}$
$[M(B3)_3]^{+2}$	$[M(B3)_3]^{+3}$	$[M(B3)_3]^{+4}$	$[M(B3)_3]^{+5}$

*Coördination number four*

P.V. = 2	P.V. = 3	P.V. = 4
$[M(B1)_2]^{-2}$	$[M(B1)_2]^{-1}$	$[M(B1)_2]^0$
$[M(B2)_2]^0$	$[M(B2)_2]^{+1}$	$[M(B2)_2]^{+2}$
$[M(B3)_2]^{+2}$	$[M(B3)_2]^{+3}$	$[M(B3)_2]^{+4}$

(\* P.V. = principal valence; B1, B2, and B3 represent one attached molecule of the respective classes.)

It is apparent that inner complex compounds result from B1 molecules with elements whose principal valence and coördination number are both four, carbon being the only example, and theoretically from elements whose principal valence and coördination number are both six, no examples being known. Chelating molecules of type B2 yield inner complexes with elements whose coördination number is just twice the principal valence, that is, either six-three or four-two combinations. Fortunately for analytical purposes this is the most common case. Theoretically, molecules which chelate by two secondary valences only, class B3, would yield inner complexes only with elements of zero valence.

Similarly tridentate molecules yield the following types of compounds, one unidentate molecule either acidic (X) or coördinating (A) being necessary to fill out the coördination number of four.

*Coordination number six*

P.V. = 2	P.V. = 3	P.V. = 4	P.V. = 5
$[M(C1)_2]^{-4}$	$[M(C1)_2]^{-3}$	$[M(C1)_2]^{-2}$	$[M(C1)_2]^{-1}$
$[M(C2)_2]^{-2}$	$[M(C2)_2]^{-1}$	$[M(C2)_2]^0$	$[M(C2)_2]^{+1}$
$[M(C3)_2]^0$	$[M(C3)_2]^{+1}$	$[M(C3)_2]^{+2}$	$[M(C3)_2]^{+3}$
$[M(C4)_2]^{+2}$	$[M(C4)_2]^{+3}$	$[M(C4)_2]^{+4}$	$[M(C4)_2]^{+5}$

*Coordination number four*

P.V. = 2	P.V. = 3
$[M(C1)X]^{-2}$	$[M(C1)X]^{-1}$
$[M(C2)X]^{-1}$	$[M(C2)X]^0$
$[M(C3)X]^0$	$[M(C3)X]^{+1}$
$[M(C4)X]^{+1}$	$[M(C4)X]^{+2}$

Members of only a relatively few of these types of compounds are known.

A similar outline of compounds containing quadridentate groups can be easily made, and the number of possible types of compounds is readily seen to be enormous, but again even fewer examples are known. With our knowledge in its present state a discussion of the possible types of quinquidentate and sexadentate compounds would be of little value, although the synthesis of such compounds is by no means impossible.

The numerous gaps among the more simple compounds, bidentate and tridentate, demand our more immediate attention. While a complete and detailed compilation of the chelate compounds would be most desirable, the suggestion of Pfeiffer (194) that another great division be added to Beilstein consisting of the chelate rings has not yet been considered seriously.

The present Beilstein system is not well adapted to the purposes of the chelate compounds, as the metallic derivatives are listed under the organic materials from which they are derived. The perspective of the smaller field of the chelate rings is thus submerged by the greater mass of organic chemistry, and the finer distinctions among the chelate compounds are too easily missed. A shorter survey is therefore likely to be more useful.

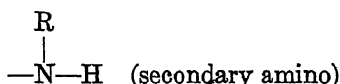
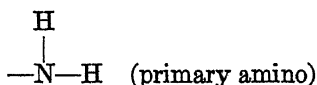
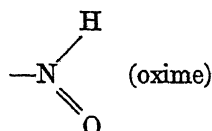
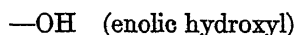
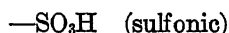
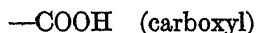
## RING STRUCTURE—ACIDIC AND COÖRDINATING GROUPS

While the chelate rings can be classified on the basis of the number of members contained in the ring, such a classification is necessarily arbitrary and more restricted than the broader one proposed above.

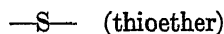
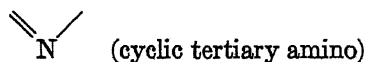
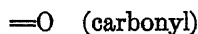
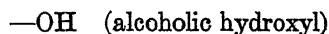
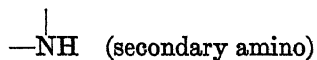
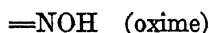
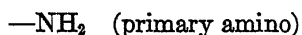
Without a doubt the number of members in the ring plays a fundamental rôle in the formation of the chelate rings, and the ultimate solution of the

subtle relations between the specificity of various organic compounds for certain metals and the structure of the molecule will rest on a consideration of the number of ring members and on their dimensions and mode of linkage. The work of Sidgwick (237) and of Pfeiffer (193, 194) has opened up the way in this direction.

Among the various organic groups which may unite with metals by the replacement of hydrogen, that is, function as acids by primary valence, the more common are the following:



As secondary valence groups which combine with metals by simple coördination or addition without the replacement of hydrogen are the following groups:



These lists could be easily lengthened but to little point, as practically all of the chelate rings known involve combinations of the functional groups given. Some of the groups behave in both ways and occasionally the function involved is difficult to determine precisely.

The various combinations of these groups will be taken up, two at a time (bidentate), considering first the combinations of two primary valences (B1), then one primary and one secondary valence (B2), and so on, as outlined in the fourth paragraph.

Combinations will be made in the order in which the groups are listed, and numbered alphabetically. Where examples are unknown the combination will simply be skipped.



## B. THE BIDENTATE COMPOUNDS

Among the chelate compounds members of the bidentate group are the longest known and the most thoroughly studied. The greater part of all the known chelate rings are of this type.

*B1. Two primary valences*

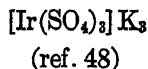
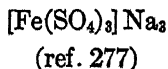
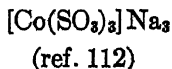
## a. Inorganic dibasic acids

Numerous compounds are known in which various dibasic inorganic anions occupy two positions in the coordination sphere surrounding a metal atom. While the carbonato compounds are perhaps the most important of these substances, since they are frequently used as starting materials in the syntheses of other coordination compounds, complexes are known in which the radicals  $\text{SO}_4^{--}$ ,  $\text{SO}_3^{--}$ ,  $\text{S}_2\text{O}_3^{--}$ ,  $\text{SeO}_4^{--}$ ,  $\text{SeO}_3^{--}$ ,  $\text{CrO}_4^{--}$ , and  $\text{MoO}_4^{--}$  occupy two coordination positions.

Four-membered rings are produced when these groups coordinate, and probably for that reason the compounds are less stable than the corresponding compounds of dibasic organic acids (see next section) which yield five- and six-membered rings. For the most part the compounds containing these chelating dibasic acid radicals contain just one such group, as in the compounds



although a few are known which contain three such rings, that is, have a coordination number of six completely filled out by bidentate groups alone:



Such compounds are usually not very stable or well defined, and exact proof of their nature is frequently lacking.

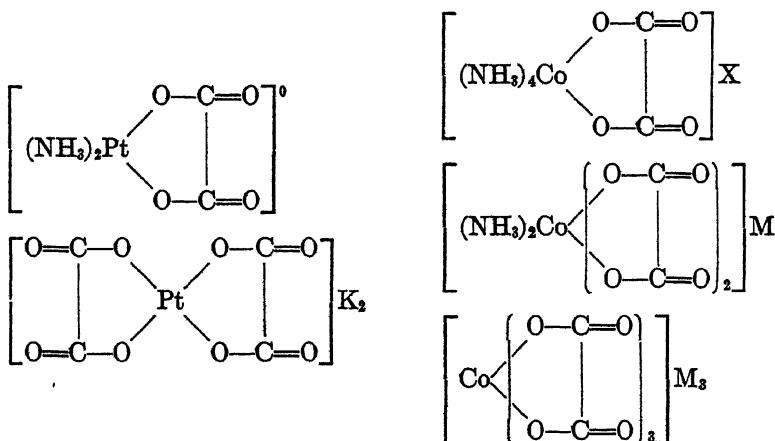
The positions in the coordination sphere occupied by these chelating groups are generally considered to be the adjacent or *cis*-positions, the groups not being large enough to span the axial or *trans*-positions. Assuming no rearrangement to occur, the replacement of these groups by two unidentate groups leads also to *cis*-compounds, and this procedure is frequently used for determining the configuration of coordination compounds.

The composition of many minerals can be neatly explained by the use

of coördination formulas involving chelate rings of this type. The recent text of Morgan and Burstall contains an excellent treatment of these minerals (178).

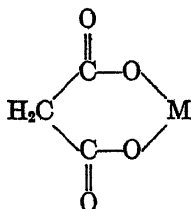
b. Two  $\text{—COOH}$  groups (organic dibasic acids)

The oxalato compounds, in which the radical of oxalic acid occupies two positions in the coördination sphere forming five-membered rings with metal atoms, are well-defined stable compounds. A great number of oxalato compounds of metals of coördination numbers of four and six are known, the metal being implicated in one, two, or three rings:



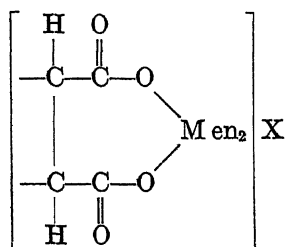
The trioxalato compounds of trivalent metals of coördination number six, —cobalt, chromium, manganese, iron, vanadium, rhodium, iridium, ruthenium, aluminum, antimony, bismuth, yttrium, etc. (110, 117, 118), —have played an important rôle in the coördination theory because of their asymmetric character, which permits resolution into optically active isomers.

Similar compounds are known with malonic acid which yields six-membered rings,



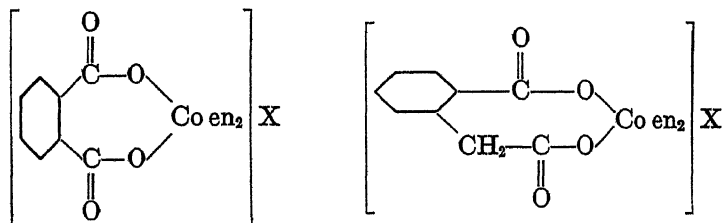
These compounds are known in the various types listed under the oxalato compounds. They are stable and well defined.

With the higher homologues which would yield rings of seven or more members no compounds are known in which a metal atom is implicated in more than one such ring. Werner (282) was unable to obtain cobalt compounds with succinic, malic, or tartaric acids. Duff later went into this question quite extensively (54). He found that the action of meso-tartaric, maleic, dibromosuccinic, itaconic, and citraconic acids on carbonato-diethylenediamino-cobalt bromide yielded crystalline compounds of the type



while *d*-tartaric, malic, mesaconic, and fumaric acids gave only viscid syrups which could not be crystallized. The carboxyl groups of the acids which gave cyclic structures are known to be in the *cis*- or neighboring positions, while in the remaining four acids the carboxyl groups are averted from each other. Succinic acid gave the typical cyclic compound only at elevated temperatures, although succinic anhydride rapidly reacted with water and the carbonato salt to give the desired compound. Succinic acid itself, although able to yield an anhydride, is regarded as having a *trans*- or fumaroid structure (54, 88).

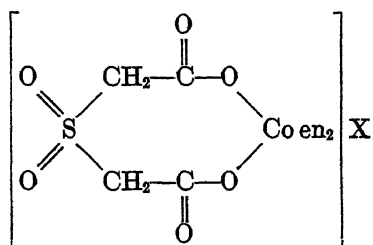
Duff (55) also found that phthalic and homophthalic acids gave crystalline compounds containing seven- and eight-membered rings.



Glutaric acid, which would give an eight-membered ring, does not yield crystalline compounds.

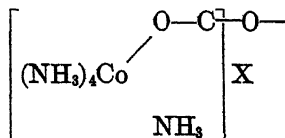
A series of copper complexes with several dicarboxylic acids and various substituted malonic acids was studied potentiometrically by Riley (213, 215). The stability of the compounds was interpreted on an electronic basis.

The first eight-membered chelate ring prepared was the ethylenediamine cobalt complex with sulfonyldiacetic acid,



prepared by Price and Brazier (205).

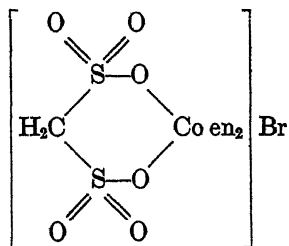
Under certain conditions only one limb of the dibasic acids may occupy a position in the coördination sphere,



Duff (56), who reviewed the methods of preparing this type of compound and extended the work to the organic dibasic acids, found the situation to be quite general, and discovered an interesting type of polynuclear compound in which two metal atoms are joined together through these acids.

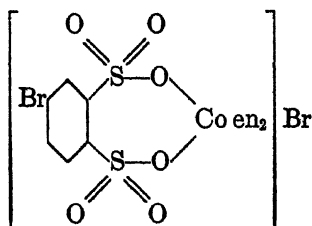
### c. Two $-\text{SO}_3\text{H}$ groups

Methiononic acid was first shown to give chelate rings by Price and Duff (206), who prepared



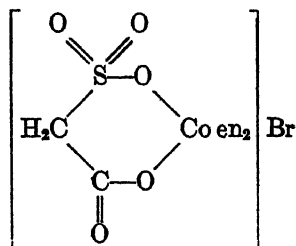
by the action of the acid on the corresponding carbonato compound.

The aromatic *o*-disulfonic acids apparently function similarly, for Duff (55) prepared



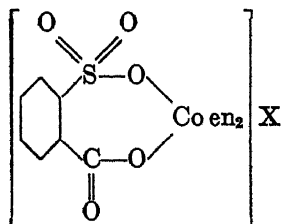
d. One  $\text{—COOH}$  group and one  $\text{—SO}_3\text{H}$  group

The action of sulfoacetic acid on carbonato-diethylenediamino-cobalti bromide was found by Price and Duff (206) to give the compound



containing a six-membered ring. Corresponding tetrammino compounds were later studied by Dubský and his coworkers (52). As would be expected, benzylsulfoacetic acid,  $\text{C}_7\text{H}_7\text{CH}(\text{SO}_3\text{H})\text{COOH}$ , gives a similar compound (55).

Sulfobenzoic acid also gives a crystalline ethylenediamine cobalt compound (55):

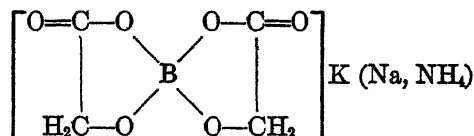


e. One  $\text{—COOH}$  group and one  $\text{—OH}$  group (both acidic)

Definite assignment of composition or structure to the metallic complexes of the aliphatic hydroxy acids is often very difficult. The weakly acidic but variable character of the hydroxyl group introduces uncertainty as to whether the hydrogen atom of the hydroxyl group has been replaced by metal or not, and as the complexes themselves frequently do not permit

isolation in the solid state their constitution is frequently left in doubt. Much of the information then comes from measurements of various types on aqueous solutions.

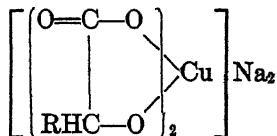
Toward boron, glycolic acid functions dibasically. The alkali metal salts of the complex acid formed,



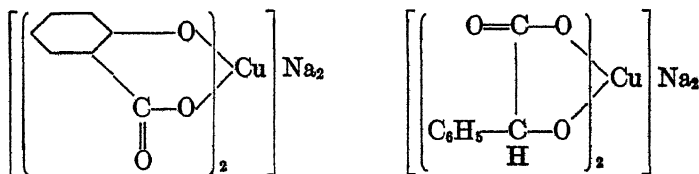
have been obtained in crystalline condition (227), and their solutions have been carefully studied by a variety of methods (29).

The study of this complex formation between the hydroxy acids and boric acid has proven fruitful in several ways. Böeseken and his students (26), by the resolution of the boron complex with hydroxybutyric acid, have furnished evidence of the tetrahedral character of the boron atom; and they have successfully applied the method to the differentiation of the *cis*- and *trans*-2-hydroxycyclopentanecarboxylic acids and similar compounds (27, 28).

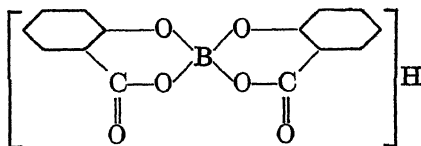
The literature on the metallic derivatives of the hydroxy acids has been carefully reviewed by Wark (270), who concluded that the complexes are more stable the more strongly the alcoholic hydroxyl group functions as an acid. The complex copper compounds of glycolic and lactic acids



are stable only in the presence of an excess of the sodium salts of the acids; the evidence for the existence of the complexes is based on potentiometric studies. The stronger acids, salicylic and mandelic, give stable crystalline complexes (273) of the same type.



A large number of very stable cyclic metallic derivatives of salicylic acid are known. Noteworthy among them is salicylato-boric acid,

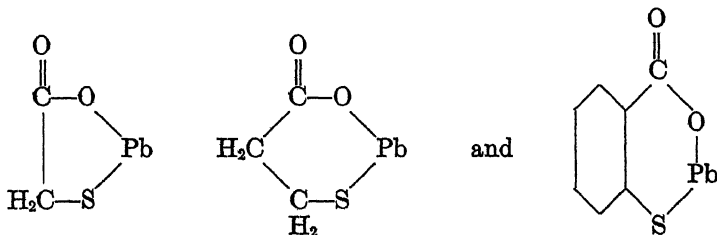


which was resolved into enantiomorphic constituents by Böeseken and Meulenhoff (24), proving that the groups are arranged around the boron atom tetrahedrally. Further studies on the various salts of salicylato-boric acid were made by Rosenheim (227). Two salicylato-ferric acids are known (280), corresponding to coördination numbers four and six.

The hydroxy and dihydroxy dibasic acids, such as malic and tartaric acids, form many very stable complexes,—for example, with copper as in Fehling's solution and with antimony as in tartar emetic. Wark has simplified this field considerably by the isolation of a number of crystalline cupri-tartrates and malates (189, 271, 272, 274), but the structure of these compounds is not yet entirely clear.

f. One  $\text{—COOH}$  group and one  $\text{—SH}$  group (both acidic)

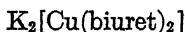
A number of metallic derivatives of thioglycolic and various other sulfhydrylcarboxylic acids are known in which the organic acid functions dibasically, for example, the lead salts of  $\alpha$ -sulfhydrylpropionic acid (12),  $\beta$ -sulfhydrylpropionic acid (122), and  $\alpha$ -sulfhydrylpropionic acid (12):



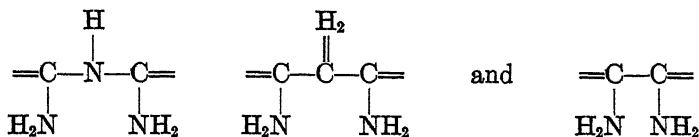
The coördination sphere of the lead atom does not appear to be filled in these cases.

g. Two  $\text{—CONH}_2$  groups (both acidic). The Biuret reaction

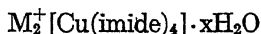
The red color produced by the interaction of biuret,  $\text{H}_2\text{NCONHCONH}_2$ , with cupric salts in alkaline solution was first observed by Wiedmann in 1848 (288). The reaction was later shown to be characteristic of proteins and many other substances (220, 221). Schiff, who carried out an extensive series of studies on the reaction (231), isolated the compound



He classified the materials which gave the reaction into three classes depending on their similarity to (1) biuret, (2) malonamide, and (3) oxamide. The arrangements of atoms typical of these groups are, respectively,

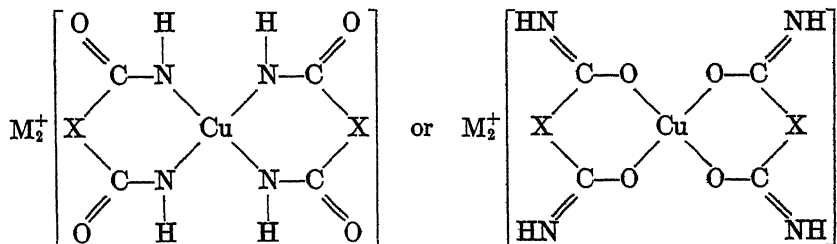


The double bonds may unite the carbon atoms to oxygen or sulfur, the compounds then functioning as dibasic acids. When the double bonds combine imino groups with the carbon atoms (iminobiuret, diiminobiuret) the compounds function monobasically, yielding non-electrolyte compounds (see B2, e). While the structures involved here are obviously cyclic, some interesting preliminary clarifying work was carried out on analogous unidentate compounds, namely on succinimide by Tschugaeff (255), phthalimide by Ley and Werner (142, 143), and barbituric acid by Rising and her collaborators (217), all of which yield compounds of the general type



Rising (216, 217) has reviewed the work on the biuret reaction and applied the test to various substituted derivatives in an attempt to find the essential features of the reaction. The imino group of biuret is considered to play no part in the reaction, since malonamide, in which it is replaced by  $\text{CH}_2$ , and oxamide, in which it is absent, give the reaction. Substitution of one or both of the hydrogen atoms of the methylene group has no effect. In oxamide the substitution of one hydrogen atom of each amino group is permissible, but when both hydrogen atoms of one amino group are replaced the test fails. With malonamide and biuret a single substitution of amino hydrogen has no effect, but symmetrical disubstitution (one hydrogen of each amino group replaced) stops the reaction; this, however, is probably due to the decreased acidity caused by the separation of the acid groups (compare the strengths of oxalic and malonic acids).

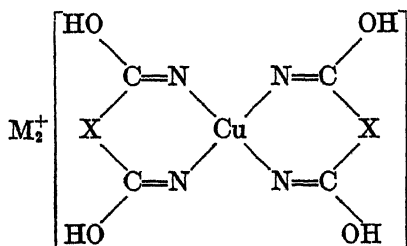
Whether the active form of the compounds is the acid amide or the acid imide tautomer cannot be decided with certainty, but the complexes undoubtedly have the structure



(where X = NH or  $\text{CH}_2$ , or is absent).



Replacement of the hydrogen of the imino group is also possible.

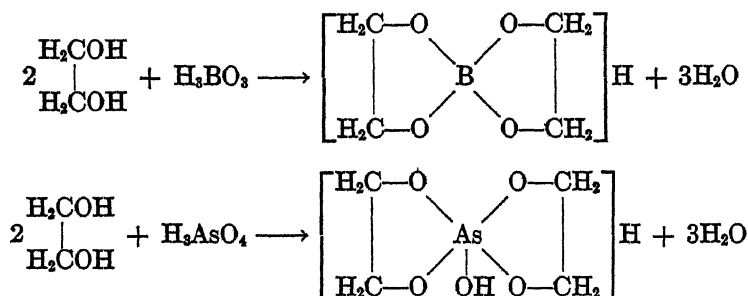


These formulas were originally proposed by Tschugaeff (255), and have been accepted by Ley (143), Kober, and others. Kober (125, 126) has extended this type of formulation to the copper derivatives of the polypeptides, but as these are probably polydentate molecules they will be discussed later. For other views on the structure of biuret compounds see the work of Traube (251) and of Jesser (116, 146).

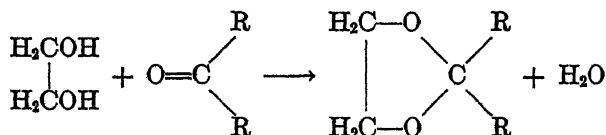
#### h. Two —OH groups (both acidic)

The great difference in the acidic character of the hydroxyl groups of aliphatic and aromatic compounds sharply differentiates the character of their compounds with the metals. While ethylene glycol shows little acidic behavior toward the metals, *o*-dihydroxybenzene acts as a dibasic acid, forming numerous well-defined chelate compounds.

The glycols do act acidic toward the non-metallic elements, especially boron and arsenic, however, although the reaction is more of the nature of esterification than of salt formation.

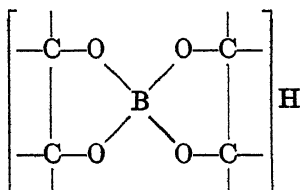


These reactions are similar to the action of the glycols on aldehydes or ketones:

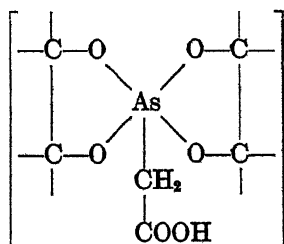


The mutual effects of the interaction of polyhydroxy alcohols and boric acid have been known for a long time. There is an enormous rise in the optical activity of the alcohol if it be active, and the acidity and electrical conductivity of the solutions undergo great increases. In the presence of glycerol or mannitol, boric acid becomes a fairly strong monobasic acid and can be readily titrated with bases. On closer study of this problem Böeseken (21) found that the position of the hydroxyl groups had a great influence on the effect produced; hydroxyl groups on neighboring carbon atoms and in the same plane produced the maximum increase in the conductivities of boric acid solutions. This immediately became very useful in the determination of the configuration of the sugars (2), diols (150, 99, 30), and other polyhydroxy compounds of various types (1, 85, 31).

Although solid compounds of this type have been isolated (90, 99), proof of their structure rests largely on evidence obtained from solutions (29, 23). The composition of the complexes is undoubtedly



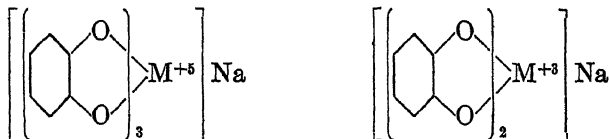
The action of the diols on arsenic acid, while not so clean cut as on boric acid, has a direct bearing on the structure of the glycols. Englund (65) found that various glycols exerted different effects on the solubilities of arsonic acids, particularly arsinoacetic acid, in 99 per cent acetic acid. The 1,2-glycols exert a pronounced effect, 1,3-glycols less; stereoisomers (racemic, active, and meso forms; *cis*- and *trans*-forms of cyclic diols) behave very differently; but variations in substituents exert relatively small effects. A number of hydroxy compounds were studied and the results can be interpreted only on the basis of ring formation of the type



It has been known for some time that the presence of polyhydroxy compounds frequently prevents the precipitation of metallic hydroxides by caustic alkalis. The nature of the complexes formed is little known.

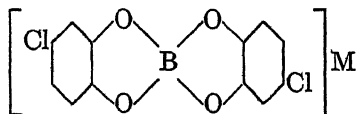
Traube (248, 249, 250) has recently isolated alkaline-earth salts of the iron complexes with mannitol, sorbitol, and a number of other hydroxy compounds. Cryoscopic and conductivity measurements are lacking on these compounds, however, so that it is difficult to assign definite structural formulas. The complexes are probably polydentate in character, the iron being attached to the alcohol through three or more hydroxyl groups.

The more acidic character of the aromatic hydroxyl group leads to more definite and stable metallic derivatives. The simplest of the diphenols, pyrocatechol, furnishes a long list of stable, well-defined compounds with metals of coordination numbers both four and six. Weinland (278, 279) obtained compounds of pentavalent arsenic and antimony (coordination number six), and Rosenheim (225) prepared the corresponding compounds of trivalent arsenic, antimony, and bismuth.

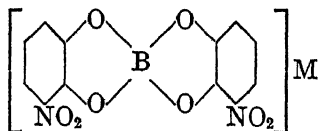


Definite proof of the structure of the tripyrocatechol arsenic (+5) complex was given by Rosenheim and Plato (226), who resolved the compound by means of cinchonine. They were able to obtain the active alkali metal salts and even the active free acid.

The substituted pyrocatechol boron complexes

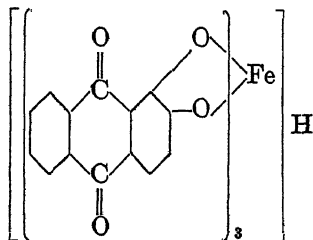


and



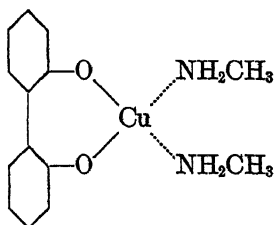
were resolved into their optically active components by Böeseken and Mijs (25, 22), proving the tetrahedral character of the quadricovalent boron atom.

Alizarin similarly forms metallic derivatives. Weinland and Binder (275) prepared various alkali metal salts of the complex acid with ferric iron



and related these to various mordant dyestuffs.

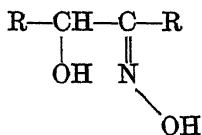
Several chelate cupric compounds of 2,2'-biphenol were obtained by Brady and Hughes (34). In some of these the biphenol apparently acted as a monobasic acid (see B2, g), but at least in di(methylamino)-cupric biphenol



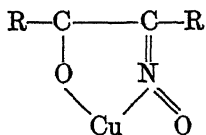
the biphenol behaved as though it were dibasic. The seven-membered ring produced here is probably non-planar, in view of the work on the stereochemistry of the ortho-substituted biphenyls.

- i. One —OH group and one =NOH group (both acidic)

The  $\alpha$ -acyloin oximes of the general formula



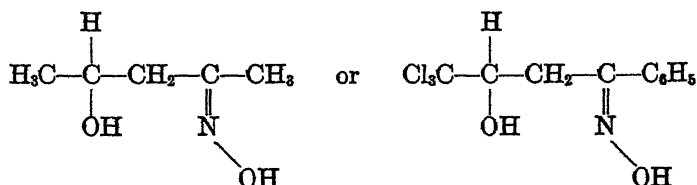
behave toward copper as dibasic acids, yielding green, insoluble, cupric salts:



Feigl and his students (77, 73) have investigated a number of these compounds for their utility in the analysis of copper, and have studied the

effects of various substituents on the color and solubility of the copper salts. Feigl has designated the  $\alpha$ -acyloin oximes as a "copper-specific" group.  $\alpha$ -Benzoin oxime is the reagent of the group most widely used. Knowles has found that it precipitates molybdenum (124) quantitatively also. The reagent also precipitates nickel and cobalt, at least under certain conditions (114), but the compounds are of a different type (see B2, 1).

When the two active groups are separated by an intervening carbon atom as in

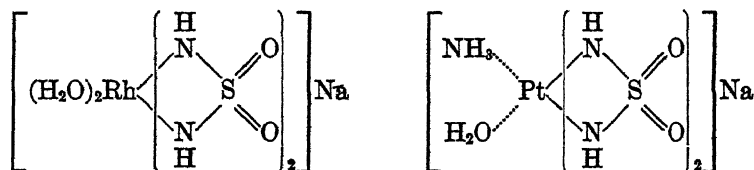


the activity toward copper is lost (75).

$\beta$ -Benzoin oxime, the stereoisomer having the oxime hydroxyl group directed toward the alcoholic hydroxyl group, forms a gray-brown copper salt, insoluble in water but soluble in ammonia and obviously having a constitution entirely different from that of the  $\alpha$ -benzoin oxime copper compound (167).

#### j. Two $\text{—NH}_2$ groups (both acidic)

Rhodium and platinum compounds of sulfamide,  $\text{O}_2\text{S}(\text{NH}_2)_2$ , were prepared by Mann (157), in which the sulfamide functions as a dibasic acid,

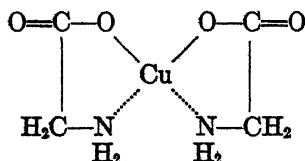


Like cobalt, rhodium and platinum (quadrivalent) have the coördination number six. The metals appear capable of taking up only two molecules of the sulfamide, however, the remaining coördination positions being occupied by unidentate groups. This behavior of sulfamide is very much like that of dimethylglyoxime toward cobalt.

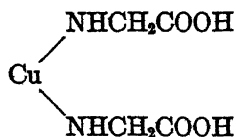
Mann was able to resolve the rhodium compound using phenylethylamine, and in this way proved that the complex ion must have a *cis*- rather than a symmetric *trans*-structure.

*B2. One primary valence and one secondary valence***a. One —COOH group (acidic) and one —NH<sub>2</sub> group (coördinating)**

The metal salts of the amino acids were the first of the inner complexes to be recognized as such. The cyclic character of copper glycine was appreciated simultaneously by Bruni and Fornara (39, 38) and by Ley (134). The compound had already been shown to be slightly dissociated and monomolecular by Curtius (44, 45), using the freezing-point method. The electrical conductivity of the compound was found to be practically negligible; for example, at a dilution of 256 liters the equivalent conductance is 0.90. The color of the compound is practically identical with that of the copper ammoniates. The compound is apparently coördinatively saturated, as it takes up very little ammonia giving a barely perceptible color change. These facts can only be explained by assuming both carboxyl and amino groups to be linked to copper as in

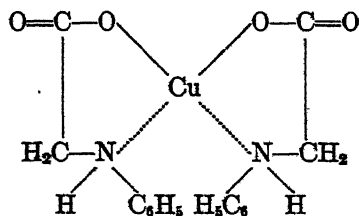


The possibility of linkage of copper to nitrogen by replacement of one amino hydrogen atom



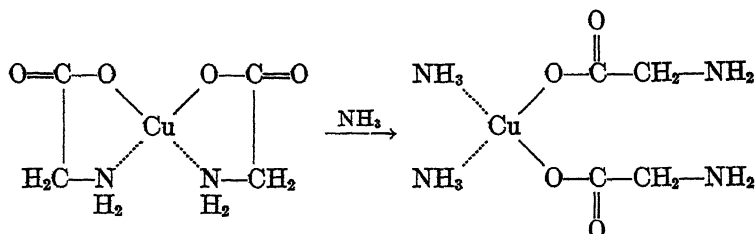
is ruled out for the dialkylated derivative, in which both hydrogens of the amino group have been substituted, forms analogous compounds (134).

The introduction of aliphatic or aryl groups into the methylene group changes the color of the metallic derivatives but slightly. An aryl substitution in the amino group, however, brings about a great change in color. Thus the copper compound of phenylglycine

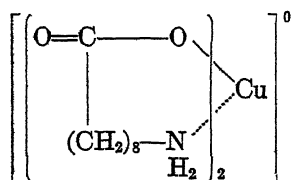


is grass-green in color, although very similar in color to the aniline complex with cupric acetate,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_6\text{H}_5\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$  (134). The light absorption of these and numerous similar compounds was extensively studied by Ley (135, 133, 144, 138).

While the dissociation of these compounds is very slight and nearly all the reactions of the metals fail on their solutions, it is nevertheless definite. Boiling alkalis gradually deposit cupric oxide, and ammonia slowly causes ring opening (133):

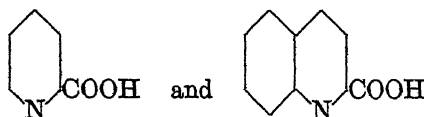


The  $\beta$ -amino acids similarly form cyclic compounds with metals, a six-membered ring then being present. When the amino group is farther removed, however, as in the  $\gamma$ -,  $\delta$ -, or  $\epsilon$ -amino acids chelation does not occur, the seven-, eight-, or nine-membered rings which would be produced apparently being impossible (266). In view of the more recent work on the higher membered rings it might be expected that polymembered chelate rings might exist. This was tested by Pfeiffer and Lübke (199) with  $\omega$ -aminopelargonic acid, which would form the twelve-membered ring:



They found no tendency for such ring formation to occur.

The acids with adjacent cyclic nitrogen atoms similarly form rings with the metals. Among these,  $\alpha$ -picolinic and quinaldinic acids



are characteristic. Several other acids of this type have been studied (140), and their unique reactions with ferrous iron observed.

A number of interesting applications to the stereochemistry of the metals have been made with the members of this group. In a planar arrangement of four covalences *cis-trans* isomerism should be observed. This has not been found with nickel or copper, but has been observed with platinum (94, 203) and palladium (203).

The cobalt and chromium compounds with the amino acids are known in two isomeric modifications (144, 145, 136) corresponding to *cis-cis* and *cis-trans* configurations about the octahedrally arranged sexacovalent metals. The determination of the configuration of these isomers has been handicapped by their completely saturated character. The introduction of optically active acids into the complexes has thrown some light on the subject and has given rise to some very interesting cases of optical activity involving partial asymmetric syntheses (137, 141, 164, 4).

A potentiometric study of the effects of alkyl substitution on the tendency of aminoacetates to coördinate with copper was made by Riley and Gallafent (214).

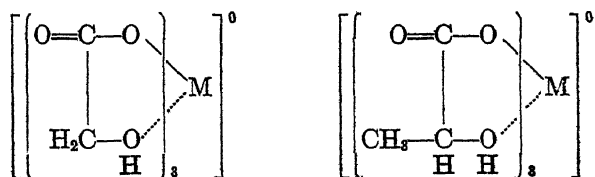
b. One  $\text{—COOH}$  group (acidic) and one  $\text{—OH}$  group (coördinating)

As pointed out in section B1, e, the precise differentiation of the metallic derivatives of the aliphatic hydroxy acids into these groups is difficult because of the variable character of the hydroxyl group, which may function in ring formation either as an acid or simply by coördination. Analytical data on crystalline compounds indicate that in the boron compound of glycolic acid the hydrogen atoms of both groups are replaced, but in the rare-earth glycolic acid compounds only one hydrogen atom is replaced.

The rare-earth salts of glycolic and lactic acids were prepared by Jantsch (113, 111). The equivalent conductance of these compounds is markedly lower than that of the corresponding acetates or phenylacetates, e.g.,

	$\nu$	
$\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3$ (acetate) .....	1024	89.5
$\text{La}(\text{C}_2\text{H}_3(\text{C}_6\text{H}_5)\text{O}_2)_3$ (phenylacetate) .....	1200	91.2
$\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3$ (glycolate) .....	1200	70.3
$\text{La}(\text{C}_3\text{H}_5\text{O}_2)_3$ (lactate) .....	1024	54.1

While the conductivities in the last two cases are far greater than that of a typical inner complex compound such as copper glycine, the values are much lower than those of the first two strictly normal salts, indicating that there occurs at least partial chelation of the type





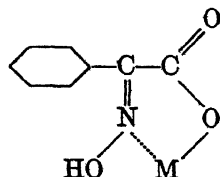
Replacement of the hydrogen atom of the hydroxyl group by methyl or phenyl does not change the properties of the compounds. As would be expected, aqueous solutions of these salts give the normal reactions of the metals.

Similar views on the constitution of the metallic salts of the hydroxy acids had been put forward earlier by Ley (135, 139) on the basis of conductivity measurements of Calame (40).

Further evidence along these lines has been recently reported by Riley and his students (78).

c. One  $\text{—COOH}$  group (acidic) and one  $\text{=NOH}$  group (coördinating)

Metallic compounds of the oxime of phenylglyoxylic acid have been reported by Hieber and Leutert (102). Of the two forms of the compound the less stable  $\alpha$ -form yields complexes with metallic salts very slowly, being converted at the same time to the  $\beta$ -form. The  $\beta$ -modification reacts instantly, yielding complexes which are formulated:

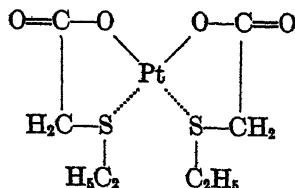


The  $\beta$ -form of the chelating molecule undoubtedly has the *syn*-phenyl configuration.

For a further discussion of the members of this group, with particular reference to hydrogen bonding, the reader is referred to the monograph of Meisenheimer and Theilacker (169).

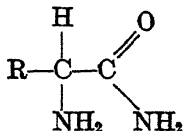
d. One  $\text{—COOH}$  group (acidic) and one  $\text{—S—}$  group (coördinating)

A platinum compound of ethylthioglycolic acid was prepared by Ramberg (207) and shown to have a cyclic structure of the type

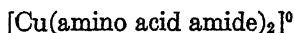


e. One  $\text{—CONH}_2$  group (acidic) and one  $\text{—NH}_2$  group (coördinating)

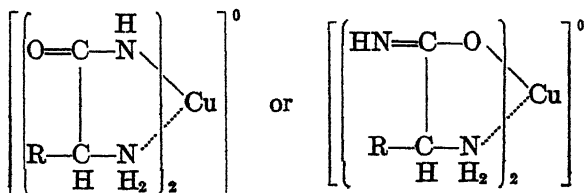
During a series of studies on the biuret reaction, Rising (219, 291) found that amino acid amides



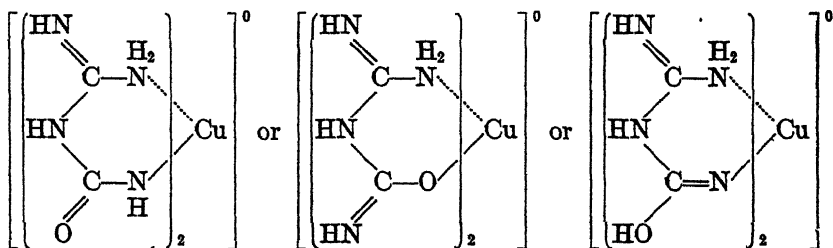
formed copper compounds, with or without the aid of alkali, the products having the composition



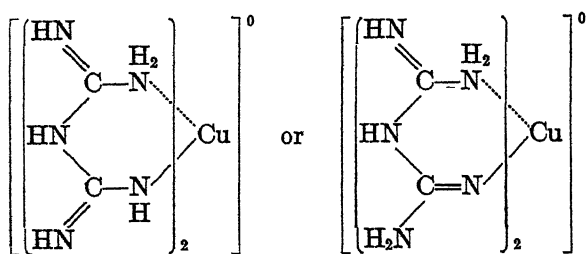
The compounds were isolated as red amorphous powders, definite in composition and stable toward water. Their solutions are non-conducting, proving their non-electrolyte inner complex character. Whether hydrogen has been replaced from the amide group or from the hydroxyl group of the tautomeric imide form has not been established, but undoubtedly the compounds correspond to one of the following structures:



Monoiminobiuret,  $\text{H}_2\text{NCONHC}(\text{:NH})\text{NH}_2$  (guanylurea or dicyanodiamidine), and diiminobiuret,  $\text{H}_2\text{NC}(\text{:NH})\text{NHC}(\text{:NH})\text{NH}_2$  (biguanidine), yield the same sort of copper compounds (89, 6), where at least in the case of diiminobiuret the metal must be linked to nitrogen. While



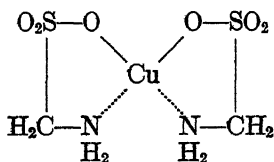
Copper monoiminobiuret

Copper diiminobiuret<sup>4</sup>

these compounds may possibly be regarded as biuret compounds, they are non-electrolytes and different in character from the typical biuret compounds (B1, g).

f. One  $\text{—SO}_3\text{H}$  group (acidic) and one  $\text{—NH}_2$  group (coördinating)

The copper salt of aminomethylenesulfonic acid is deep blue in color like copper glycine and is assigned the chelate structure



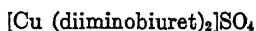
The salt is far more extensively dissociated than the copper salt of glycine, however (171). The copper salt of aminosulfonic acid,  $\text{H}_2\text{NSO}_3\text{H}$ , has a normal composition.

- The compounds of corresponding aromatic acids were studied by Pfeiffer (192).

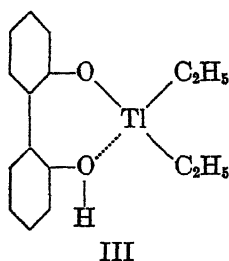
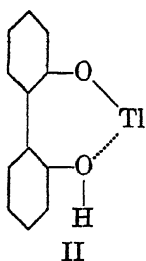
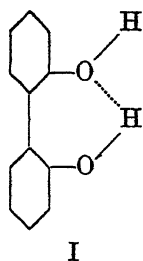
g. Two  $\text{—OH}$  groups (one acidic and one coördinating)

Considerable evidence points to the fact that 2,2'-biphenol (I) is itself coördinated (34). The univalent thallium (II) and diethyl-thallium (III) derivatives are also apparently coördinated compounds,

<sup>4</sup> Diiminobiuret tends to form the compound



where chelation occurs by two secondary valences (209,100) and gives the above compound only when treated with alkali; the compound separates free of alkali metals, however.

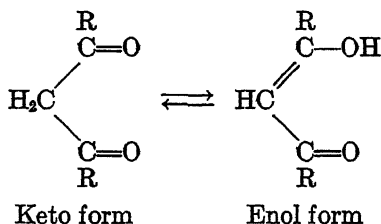


although the thoroughly saturated character of the inner complexes (non-electrolytes) here is not so completely borne out. Biphenol also acts as a bidentate chelating group in classes B1 and B3.

h. One —OH group (acidic) and one =O group (coördinating)

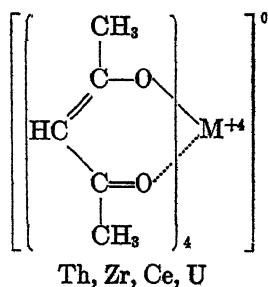
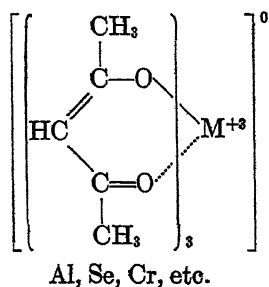
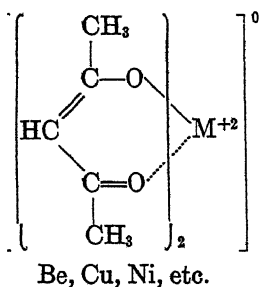
In this group of compounds fall the metallic derivatives of the 1,3-diketones, the aromatic *o*-hydroxyaldehydes, and the *o*-hydroxyphenones.

The 1,3-diketones form metallic compounds by virtue of their ability to enolize:

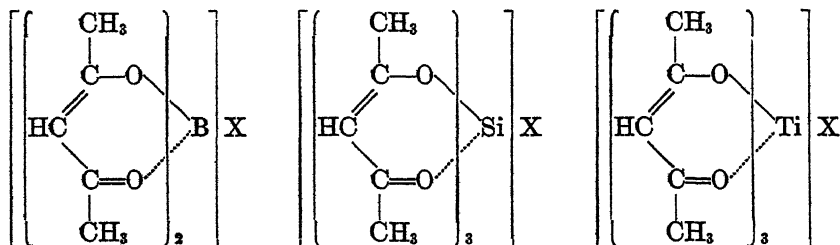


Although numerous metal derivatives of the simplest member, acetylacetone (both R = CH<sub>3</sub>), had long been known, their cyclic character was first pointed out by Werner in 1901 (283).

The acetylacetonates of practically all of the metals have been prepared (183). Most are of the non-electrolyte type



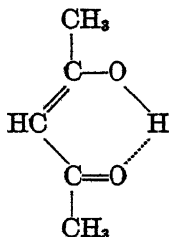
and are insoluble in water, soluble in non-polar solvents, etc. Their stability is exceptional; many can be distilled without decomposition at temperatures ranging to over 300°C., which has led Morgan to remark (181) that acetylacetone has given wings to the metals. Among the metals whose principal valence does not happen to be just half of the coördination number, the acetylacetonates of boron, silicon, and titanium prepared by Dilthey (49, 50) should be mentioned.



Acetoacetic ester and its analogues are members of this group, and their copper derivatives, used by Hieber (101) in determining the extent of enolization of these compounds, are inner complexes.

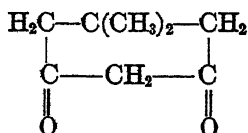
The relative stability of the copper compounds has been found to parallel the percentage of enol form in the pure compounds (174).

Sidgwick (238) concluded from chemical and physical properties that the enol form of the 1,3-diketone is mainly if not wholly a cyclic structure in which hydrogen is coördinated to the carbonyl oxygen.



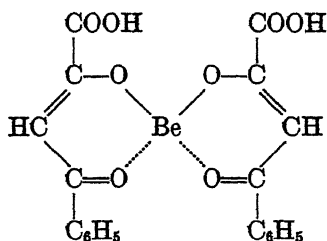
Characteristic —OH absorption in the infra-red is lacking in these compounds (107), and this is further evidence for such chelation or hydrogen bonding.

The cyclic diketone 5,5-dimethylcyclohexanedione-1,3



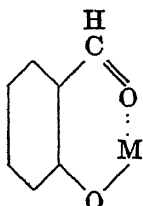
does not yield metallic derivatives of the type just discussed (286), nor are the physical properties of the pure diketone like those of the aliphatic, readily enolizable diketones.

Among the interesting applications of the 1,3-diketones to the stereochemistry of the metals may be mentioned the benzoylpyruvic acid derivative of beryllium.



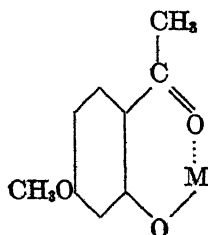
The brucine salt of this complex was found by Mills and Gotts (172) to exhibit definite mutarotation, which is considered to be definite proof of the tetrahedral character of the beryllium atom.

Numerous metal compounds of salicylaldehyde are known of the following type:



In general they are formed in organic solvents and do not appear to be very stable toward water.

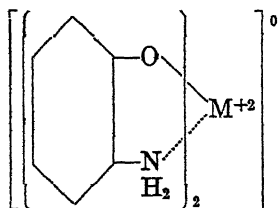
The *o*-hydroxyacetophenones are also capable of yielding complexes with the metals, for Pfeiffer (197) has prepared the cobalt, copper, and nickel derivatives of *p*-methoxy-*o*-hydroxyacetophenone (pāonol), which are typical inner complex compounds.



i. One —OH group (acidic) and one —NH<sub>2</sub> group (coördinating)

Hieber and Levy (103) have recorded divalent cobalt compounds of monoethanolamine in which part of the attached ethanolamine molecules in the complex chelate by replacement of the hydroxyl hydrogen atom. The compounds are formed only in alcohol, and the situation is further complicated by the formation of polynuclear compounds. The nickel, copper, and zinc compounds were also studied (104); the greater tendency seems to be for the ethanolamine to chelate by two secondary valences, however.

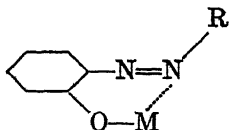
As would be expected, the aromatic compounds, in which the hydroxyl group is much more acidic, furnish more definite, stable compounds (106). The *o*-aminophenol derivatives of copper, nickel, zinc, and cadmium



are typical inner complex compounds.

j. One —OH group (acidic) and one —N=N— group (coördinating)

In the course of a study of the chelate rings formed in mordant dyeing, Morgan (185) showed that in the azo dyestuffs containing an *o*-hydroxyl group, mordanting took place with the formation of chelate rings, the metal being attached by secondary valence to the azo group



Such ring formation cannot occur when the hydroxyl group is in the meta- or para-positions, and this is in accord with the long-established rule that such compounds are never dyestuffs.

More recently Elkins and Hunter (58) have found that the formation of cupric, nickel, and cobaltic compounds is characteristic of all *o*-mono-hydroxyazo compounds and that such formation occurs readily by the action of the metallic acetates on the azo compound. The salts correspond to the formulas R<sub>2</sub>Cu, R<sub>2</sub>Ni, and R<sub>2</sub>Co, R being the molecule of the *o*-hydroxyazo compound minus one hydrogen atom. The salts are typical inner complexes (non-electrolytes); they are insoluble in water and polar

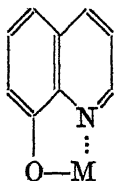
solvents, but readily soluble in non-polar solvents. They are very stable, melting in the neighborhood of 200°C. without decomposition to form deeply colored liquids.

The existence of these compounds is interpreted as evidence that the geometrical arrangement of the groups attached to the azo group is *trans* (58). Absorption spectra data also indicate that the hydroxyl hydrogen atom of these *o*-hydroxyazo compounds is coördinated to the azo group.

The blue magnesium lake with *p*-nitrobenzeneazoresorcinol which is used as a qualitative test for magnesium (244, 228, 64) is undoubtedly due to chelation of this sort.

k. One —OH group (acidic) and one  $\text{N}=\text{N}$  group (coördinating)

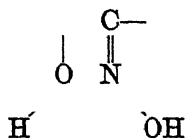
Numerous metallic derivatives of 8-hydroxyquinoline are known of the general chelate type



These salts were suggested for analytical purposes by Hahn (95) and Berg (15) in 1926; since then they have undergone very rapid development and are now extensively used. Berg (16) has contributed a monograph dealing exclusively with the applications of 8-hydroxyquinoline to analytical chemistry.

l. One —OH group (acidic) and one =NOH group (coördinating)

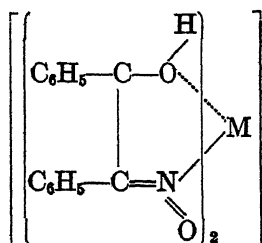
Two types of compounds, both containing as functional groups a hydroxyl group and an oxime group, have been found to yield insoluble compounds with copper. In the acyloin oximes, investigated by Feigl (69, 77, 72), the characteristic atomic grouping is



Toward copper these compounds act as dibasic acids, both hydrogens being replaced by the metal, and therefore they were discussed under class B1. Jennings, Sharratt, and Wardlaw (114) found, however, that  $\alpha$ -benzoin

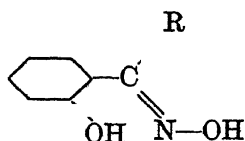


oxime functions toward nickel, palladium, and divalent platinum as a monobasic acid, giving typical inner complex compounds of the formula:



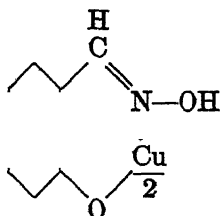
These compounds exist in two mutually interconvertible forms, but the nature of this isomerism has not yet been explained. Still another nickel derivative of  $\alpha$ -benzoin oxime was obtained in which the oxime formed the chelate rings by coördinating valences alone (see B3, e).  $\alpha$ -Benzoin oxime thus functions as a bidentate molecule in all three classes.

The other copper-specific group is that of the aryl aldoximes and aryl ketoximes containing an *o*-hydroxyl group

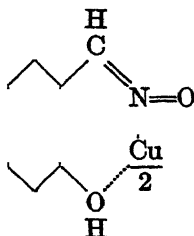


Salicylaldoxime, the simplest member of the class, was first employed as an analytical reagent for copper by Ephriam (66). A further investigation by Ephriam (67) showed that this ability to precipitate copper from acetic acid solutions was not destroyed by the introduction of substituents into the phenyl group or in place of the aldehyde hydrogen atom.

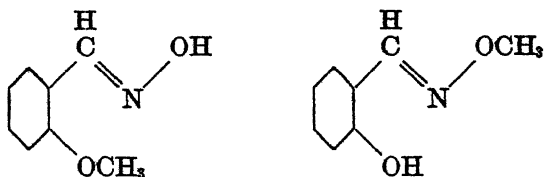
Ephriam preferred to formulate the copper compound as



the hydrogen of the —OH group being replaced by the metal. Feigl (75), after pointing out that the principal valence linkage might equally well be to the oxime group,

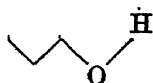
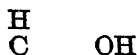


prepared the two methyl ethers of salicylaldoxime

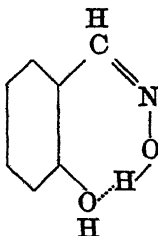


and found that only the compound with the free  $-\text{OH}$  group (the oxime ether) gave a copper compound. Feigl interprets this as support for the Ephriam formulation in which the hydroxyl hydrogen is replaced by the metal atom.

The *anti*-phenyl form of salicylaldoxime has been assumed to be present in all of these complex formation reactions and, indeed, in view of the great amount of evidence accumulated in the field of the oximes of the  $\alpha$ -diketones (see B2, o and p) this is undoubtedly correct. Brady (33) has also brought forward several arguments in favor of hydrogen-bond formation through the hydroxyl hydrogen atom

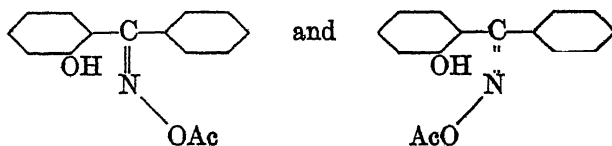


rather than through the hydrogen of the oxime group



in salicylaldoxime itself.

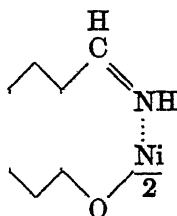
This has been more recently confirmed by infra-red absorption measurements (98). Again, of the two acetates (19, 127) of 2-hydroxybenzophenone oxime



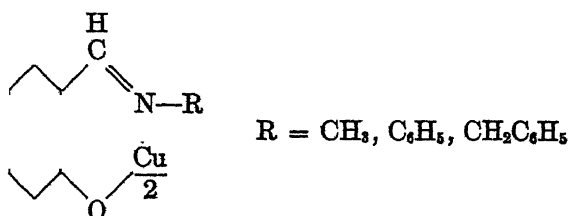
only the isomer in which the —OAc group is toward (*cis* to) the phenolic —OH gives characteristic —OH absorption (98). Hydrogen bonding is evidently present in the *trans*-isomer. Meisenheimer (168) has also shown that of the two forms only the *trans*-form yields complex salts with nickel.

m. One —OH group (acidic) and one =N—R group (coördinating)

The action of nickel salts on *o*-hydroxyaldehydes in aqueous ammonia solutions leads, surprisingly enough, to the nickel salt of hydroxyaldimines



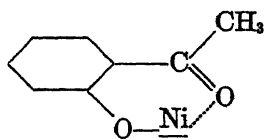
in which the aldehyde oxygen atom has been replaced by =NH. Pfeiffer (196) and his coworkers, who stumbled onto this, found on surveying the literature that such a reaction had been observed as far back as 1840 by Ettling (68). Later Schiff (230) and Delépine (47) reported similar copper compounds:



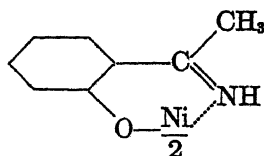
Pfeiffer found that copper, nickel, and zinc caused this same replacement, but that calcium and magnesium salts led to normal salts with no formation of imine.

With *o*-hydroxyacetophenone the replacement of the oxygen atom by

the imino group did not proceed in dilute ammoniacal solution, but went rapidly and completely on warming a solution of the nickel salt of *o*-hydroxyacetophenone in concentrated ammonia:



(greenish-yellow)

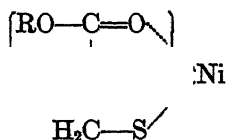


(dark red)

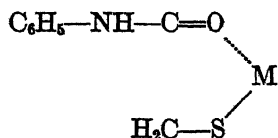
n. One —SH group (acidic) and one =O group (coördinating)

The acidity of the —SH group of thioglycolic acid,  $\text{HSCH}_2\text{COOH}$ , overshadows the acidic behavior of the carboxyl group. There is some indication that thioglycolic acid forms chelate rings by replacement of hydrogen atoms from both the —COOH and the —SH groups. More definite compounds are obtained when the acidic function of the carboxyl group is voided by ester or amide formation and the carbonyl oxygen atom can then enter into chelate ring formation by simple coördination.

The nickel derivatives of the methyl and ethyl esters of thioglycolic acid (51) are typical.



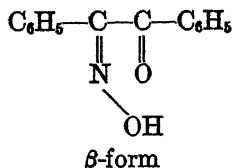
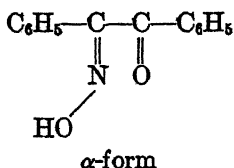
The metal derivatives of thioglycolic acid anilide are also chelate compounds



The analytical utility of these compounds has been pointed out by Berg and Roebeling (17), who advocate the use of thioglycolic- $\beta$ -aminonaphthalide (Thionalid) as a reagent for the detection and determination of various heavy metals.

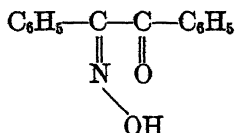
o. One =NOH group (acidic) and one =O group (coördinating)

That the stereochemical configuration of the monoximes of the  $\alpha$ -diketones governed their reactions with the metals was first recorded by Whiteley (287), who found that of the two isomeric benzil monoximes

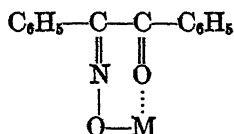


the  $\alpha$ -form yielded a deep blue ferrous compound, while the  $\beta$ -form did not. Tschugaeff extended this work to cobalt, nickel, and platinum (263). These compounds are highly stable, being unattacked by mineral acids or cyanides, and possess very striking and anomalous colors.

On the basis of the coördination theory these were immediately seen to be cyclic compounds. The configuration originally assigned to the  $\alpha$ -benzil monoxime on the basis of the Beckmann rearrangement was the *syn*-form



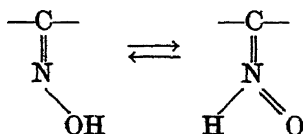
and Werner (285) assigned to its metallic derivative the structural formula



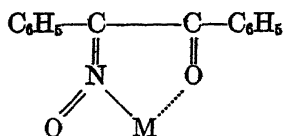
rejecting the five-membered ring earlier proposed by Tschugaeff (263, 254). This six-membered ring structure was widely accepted and appeared in the literature for some time.

The work of Meisenheimer on the oximes, however, has led to a complete reversal of the interpretation of the Beckmann rearrangement, namely, that the assumption that the rearranging groups were *cis* to each other was erroneous (166, 18). There can be no doubt now that the *trans* shift is correct and that  $\alpha$ -benzil monoxime must actually be the *trans*-isomer. The difficulty with the above formula for the metallic derivatives immediately becomes obvious.

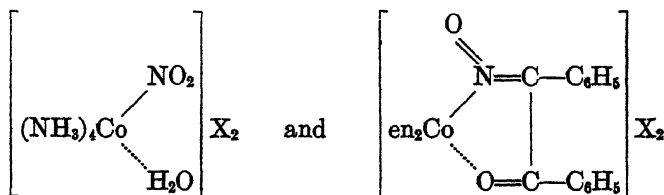
Pfeiffer and Richarz (201) resolved this problem by assuming that the tautomeric nitron form of the oximes



was responsible for formation of metallic compounds. (Brady and Mehta (35) have isolated oxygen and nitrogen ethers corresponding to each of these forms.) The hydrogen atom is replaced by metal, giving a direct metal-to-nitrogen linkage. This results in the formation of five-membered rings:



The metal-nitrogen linkage is well known among the coordination compounds, for example, the nitro cobalt ammines,  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{X}_2$  and  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{X}$ , both of which are yellow in contrast to the nitrito compounds, for example,  $[(\text{NH}_3)_5\text{Co}-\text{ONO}]\text{X}$ , which is pink in color and unstable, passing slowly into the corresponding nitro compound. Pfeiffer found that the colors of the very similar compounds

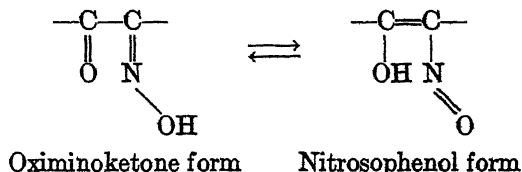


were practically identical (195).

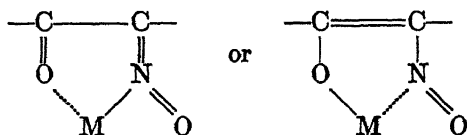
The monoximes of the  $\alpha$ -diketones give characteristic color reactions with ferrous salts. Feigl and his coworkers have investigated a series of these compounds from the standpoint of the so-called "iron blue reaction." The work has been summarized in his book (74).

The copper complex of  $\beta$ -benzil monoxime has been used to follow the interconversion of the  $\alpha$ - and  $\beta$ -forms of benzil monoxime in various solvents (245).

The nitrosophenol group is tautomeric with the diketone monoxime group

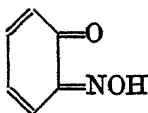


It is difficult to know which of these forms is responsible for salt formation; whether to write the formula of the metallic derivatives as

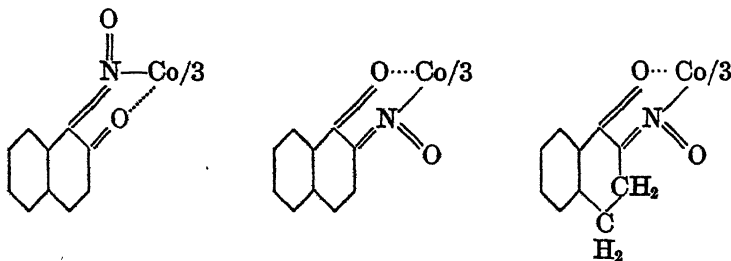


Perhaps this is a question of resonance, both forms being present.

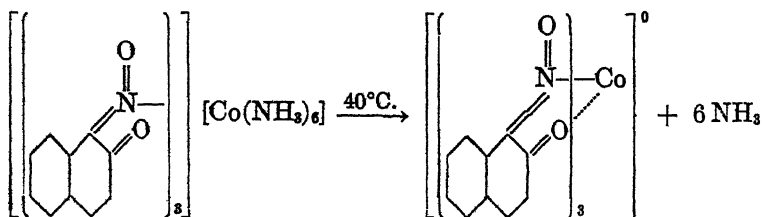
Besides simple *o*-nitrosophenol



the metallic compounds of which were investigated by Baudisch (9, 11), there also fall in this class the analytically useful cobalt reagents  $\alpha$ -nitroso- $\beta$ -naphthol (108, 163),  $\beta$ -nitroso- $\alpha$ -naphthol (13), and 2-isonitroso-1-ketotetralin (242). Formulated on the ketoxime form their cobalt derivatives may be considered to be

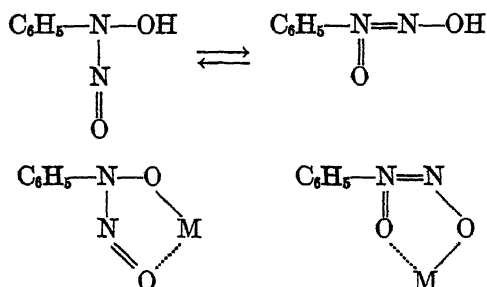


The great tendency for chelation to occur in these compounds is illustrated by a reaction carried out by Morgan and J. D. Main Smith (184), who found that the normal hexamminocobalti (luteo) salt of  $\alpha$ -nitroso- $\beta$ -naphthol on slight warming in aqueous solution rapidly expelled ammonia:



The authors further showed that the numerous derivatives of  $\alpha$ -nitroso- $\beta$ -naphthol, so extensively used as dyestuffs, owe their mordanting properties to just such ring formation as this, and that other attached groups,  $-\text{SO}_3\text{H}$ , etc., are inactive.

The analytical reagent cupferron, the ammonium salt of nitrosophenylhydroxylamine (8, 10, 5), also falls in this class. The reagent and metallic derivatives may again be written in tautomeric or resonance forms.

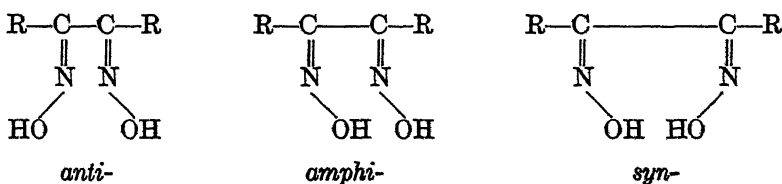


p. One  $=\text{NOH}$  group (acidic) and one  $=\text{NOH}$  group (coördinating)

The metallic compounds of the dioximes of the  $\alpha,\beta$ -diketones (substituted glyoximes) were discovered by Tschugaeff (264). In a series of investigations he studied the behavior of a number of differently substituted glyoximes against various metals. The nickel and palladium salts were always insoluble in alkaline or neutral solutions, and had the general formula  $(\text{HD})_2\text{M}$ , where  $\text{H}_2\text{D}$  represents the dioxime molecule and M the metal (256, 257). Cobalt formed soluble compounds and appeared capable of combining with only two molecules of the dioxime. Numerous cobalt compounds with the dioximes were isolated in which the remaining two coördination positions are occupied by various coördinating or acidic groups,

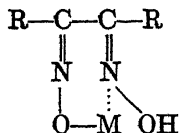
$[\text{Co}(\text{HD})_2(\text{NH}_3)_2]\text{X}$ ,  $[\text{Co}(\text{HD})_2(\text{NH}_3)\text{X}]$ , and  $[\text{Co}(\text{HD})_2\text{X}_2]\text{M}$  (252, 259)

Complex formation of the dioximes, again, is dependent on the stereochemical configuration of the oxime. Three stereoisomeric forms of the symmetrically substituted dioximes exist, corresponding to the configurations

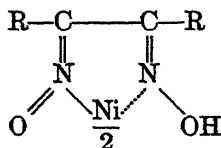




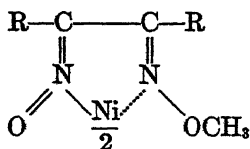
Of these the  $\alpha$ -modification yields typical, brilliant red nickel salts. The older configuration determinations assigned the *syn*-form to the  $\alpha$ -modification, and the metallic complexes were written as six-membered ring structures.



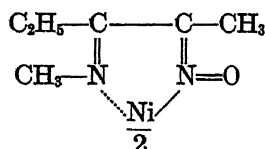
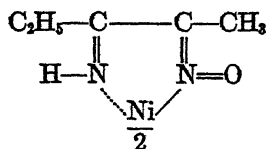
The inadequacy of this formulation on the basis of the newer configuration determinations which assign the *anti*-configuration to the  $\alpha$ -form is readily seen. Applying reasoning similar to that adapted to the monoximes, the structure of the dioximes may be represented as



involving the tautomeric nitron form of the oxime and a five-membered ring, one oxime group being bound to the metal through primary valence, nitrogen to nickel, and the other by secondary valence (102, 195). That the hydroxyl group of the second oxime plays no part and the metal is not linked to oxygen is shown by the ready formation of exactly similar complexes by the mono-*O*-ethers (246, 36, 191):



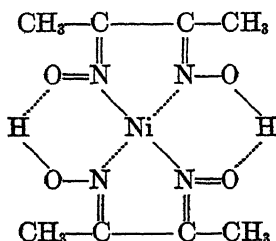
Pfeiffer has also found (191) that, when one of the oxime groups is replaced by an imino or methylimino group, complex formation occurs in identical fashion.



As mentioned, the *anti*-dioximes form stable, brilliant red compounds with nickel. Indeed, the tendency for such formation to occur is so great

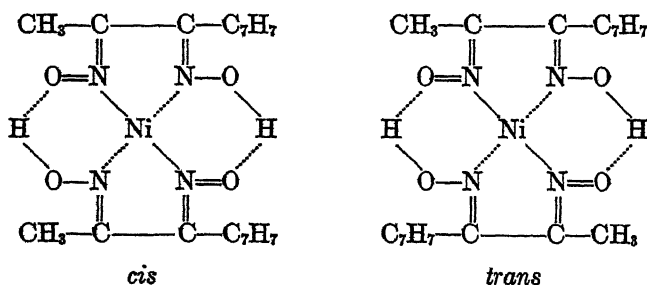


That no such isomerism has ever been observed may be explained by a tautomeric shift of the hydrogen atom (243), or, better, by assuming hydrogen bonding to occur between the neighboring oxygen atoms. Brady (36) writes the formula thus:



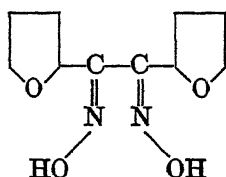
This formula also explains the lack of reactivity of the hydroxyl group in these compounds. Tschugaeff (204) found that nickel dimethylglyoxime would not react with phenyl isocyanate, and Barker (7) states that acetic anhydride has no effect on it. With methyl iodide nickel dimethylglyoxime yields an addition product from which water regenerates the original red nickel compound. Brady and Muers (36) report that nickel dimethylglyoxime gives no methane with methylmagnesium iodide in amyl ether.

The dioximes have been very useful in proving the planar structure of the quadricovalent nickel atom. Sugden (243, 41) has prepared two isomeric nickel derivatives of unsymmetrically substituted glyoximes corresponding to *cis*- and *trans*-configurations



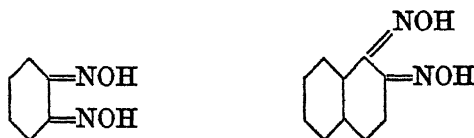
Palladium shows the same type of isomerism (57).

The practically specific action of the  $\alpha,\beta$ -dioximes in forming insoluble nickel compounds has led to their widespread use in the qualitative and quantitative analysis of nickel. The insolubility of the usual reagent, dimethylglyoxime, in water, however, is a great disadvantage. Soule (241) has found that  $\alpha$ -fural dioxime

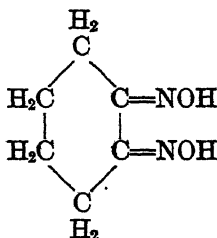


is soluble to about 10 per cent in water and, besides being more sensitive as a qualitative test, has a lower metal content. This reagent warrants more widespread use.

The specific activity of the dioxime group for nickel is lost in the unsaturated cyclic  $\alpha$ -diketone dioximes



which act as dibasic acids and form precipitates with numerous metals (70). Cyclohexanedione dioxime,

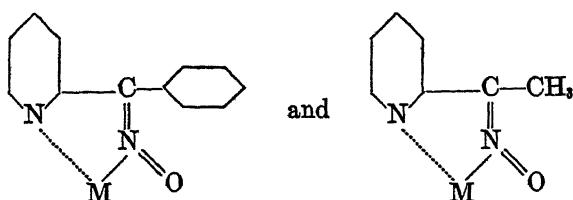


on the other hand, is again specific for nickel and more sensitive than dimethylglyoxime (269). The reagent is water-soluble and is frequently cited in papers dealing with organic analytical reagents as being the ideal organic reagent. It has not been widely adopted, however.

The dioximes of  $\alpha,\gamma$ - and  $\alpha,\delta$ -diketones do not form chelate rings with metals (261).

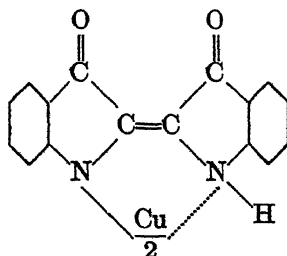
q. One  $=\text{NOH}$  group (acidic) and one  $\text{>N/}$  group (coördinating)

The complex metallic derivatives of this class were first found by Tschugaeff (254, 261), who prepared the platinum and palladium derivatives of phenyl- $\alpha$ -pyridyl oxime and formulated them as chelate compounds. The metallic compounds of methyl- $\alpha$ -pyridyl ketoxime have also been studied (60). These compounds are formulated after the Pfeiffer method (195) as

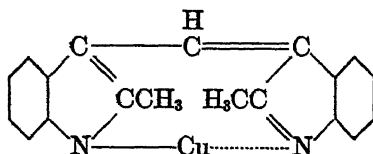


r. Two —NH groups (one acidic and one coördinating)

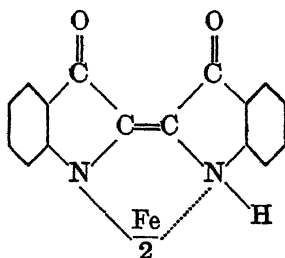
In a series of papers Kunz (129, 130, 132, 131) investigated the metallic derivatives of indigo and similar compounds, with particular reference to the bearing the compounds had on the metal-porphyrin problem. While Kunz assumed that the metals in his compounds were linked to the nitrogen atoms by secondary valences alone, careful reviews of the compounds by Kuhn (128) and by Schmitz-Dumont (233) lead to the conclusion that this assumption was wrong and that the metals unite with the dyestuff with the replacement of hydrogen. The copper derivative of indigo is then



From stereochemical considerations and other reasoning, Kuhn concluded that the metal in these compounds is attached to the carbonyl oxygen rather than to the imino nitrogen atom. Kuhn's formula is given in the next section. The compound bis-( $\alpha$ -methyl- $\beta$ -indyl)methene, in which the oxygen atoms of the indigo molecule have been removed, still yields metallic derivatives, for example, a monovalent copper compound (132, 233) in which one atom of copper is united to one molecule of the organic compound

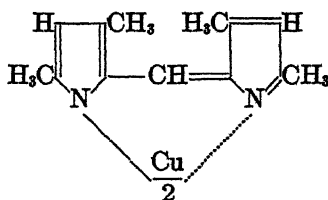


The extremely interesting iron compound of indigo was shown by Kunz and Kress (131) to exhibit a most astonishing similarity to hemoglobin. On heating iron carbonyl with indigo in pyridine, carbon monoxide is evolved and a yellowish-red compound is obtained.



A pyridine solution of this compound rapidly absorbs oxygen, the color shifting at the same time from red to green. One molecule of oxygen is added for each atom of iron. The oxygen is only loosely held, for it is released by the application of a vacuum, the color changing back to the original red. Carbon monoxide destroys this ability to take on oxygen. Chilling a solution of the green compound yields a solid which does not give up its oxygen in a vacuum and which on heating gives oxidation products of indigo. These properties are just those of hemoglobin, and the iron-indigo compound is thus a unique breathing model.

Bearing even more directly on the hemoglobin problem are the copper compounds of the dipyrromethenes, for example, of tetramethyldipyrromethene:

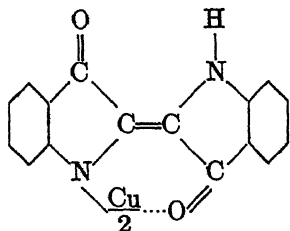


synthesized by Fischer and Schubert (84).

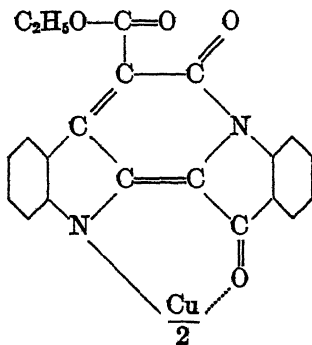
- s. One —NH group (acidic) and one =O group (coördinating)

As mentioned in the preceding section, Kuhn (128) considered the secondary valence of the metals in their complexes with indigo to be directed toward the carbonyl oxygen rather than toward the imino nitrogen atom. This is in agreement with the modern views that indigo has a

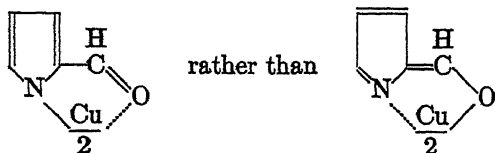
fumaroid (*trans*) structure. Chelation on a *trans* structure could then only occur from nitrogen to oxygen:



Kunz found that indigo-malonic ester also readily gave copper and cobalt compounds in which necessarily the metal is linked to nitrogen and oxygen:



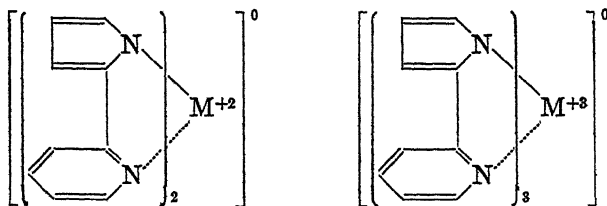
An inner complex copper compound of  $\alpha$ -pyrrolealdehyde was prepared by Emmert (61) by the action of the aldehyde on copper oxide in xylene. The compound is sensitive to water and is probably best formulated as a derivative of the aldehyde rather than its tautomeric enolic form, that is,



inasmuch as the copper derivatives of numerous enolic compounds are perfectly stable toward water. In physical properties pyrrolealdehyde itself is differentiated sharply from other aldehydes, such as benzaldehyde and furfuraldehyde.

t. One  $\text{—NH}$  group (acidic) and one  $\text{=N}$  group (coördinating)

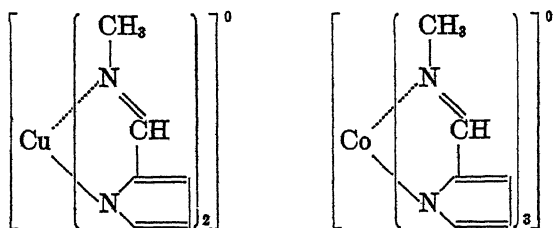
Several metallic complexes of  $\alpha$ -( $\alpha'$ -pyridyl)pyrrole were prepared by Emmert and his coworkers (59, 61). The pyrrole groups act acidic in these compounds and the copper, zinc, cadmium, nickelous, ferric, and cobaltic compounds are typical inner complexes (non-electrolytes) having the following structures:



They possess anomalous colors, and are insoluble in water but soluble in organic solvents. The zinc and aluminum compounds exhibit extremely beautiful fluorescence.

u. One  $\text{—NH}$  group (acidic) and one  $\text{=N—}$  group (coördinating)

Inner complex compounds of  $\alpha$ -pyrrolealdehyde-methylimine



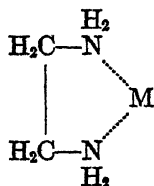
were prepared by Emmert and his students (61).

### B3. Two coördinating valences

a. Two  $\text{—NH}_2$  groups (both coördinating)

The first of the compounds which we now consider to be cyclic were the ethylenediamine complexes of platinum and cobalt discovered by Jørgensen in 1889 (119). The ethylenediamine complexes fitted beautifully into the coördination theory of Werner if the assumption was made that each of the amino groups occupied a position in the coördination sphere of the metal giving rise to a ring structure:

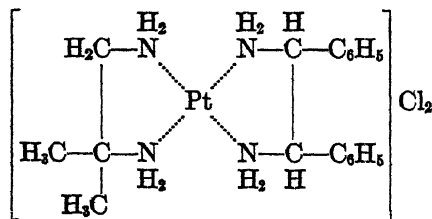




It was further assumed that the two groups of the coordinating molecule must occupy *cis*- or neighboring positions, the molecule simply not being large enough to span the *trans*- or axial positions. Assuming also that no rearrangement occurs on replacing the ethylenediamine molecule by two other groups, this furnishes a powerful method for determining the configuration of isomeric coordination compounds, and this procedure has indeed been extensively employed.

Ethylenediamine compounds with a great number of metals have been made; with cobalt alone the number of *cis-trans* isomeric pairs which have been studied approaches thirty.

The ethylenediamine derivatives played another important rôle in furnishing asymmetric complex molecules which could be resolved into optically active constituents. Indeed it was only with the optical resolution of the complexes that the coordination theory received unreserved acceptance. This field has been rather widely studied and the literature has been adequately reviewed by Jaeger (109) and by Bailar (4). A substituted ethylenediamine platinum derivative was employed by Mills and Quibell (173) in their extremely neat proof of the planar configuration of the quadricovalent platinum atom. They were able to resolve isobutylenediamino-meso-stilbenediamino-platinous chloride,



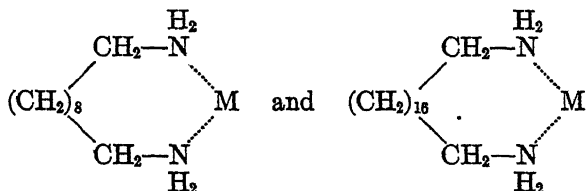
a compound which is completely asymmetric if the platinum atom has a planar configuration, but which possesses a plane of symmetry if the coordinating groups are tetrahedrally disposed.

The enormous increase in stability resulting from ring formation may be seen from a comparison of the compounds  $[\text{Ni}(\text{NH}_3)_6]\text{X}_2$  and  $[\text{Ni}(\text{en})_3]\text{X}_2$ . The former is rapidly hydrolyzed in water, as shown by its conductivity and cryoscopic behavior, its aqueous solution has a distinct odor of ammo-

nia, and at a dilution of 100 liters it yields a precipitate of nickel hydroxide; the aqueous solutions of the latter, however, are entirely normal and stable even at a dilution of 1000 liters (262).

Trimethylenediamine behaves analogously to ethylenediamine in its action toward the metals, six-membered rings being formed.

Several studies have indicated, however, that higher membered rings of this type cannot form or are extremely unstable. Tetramethylenediamine (putrescine) and pentamethylenediamine (cadaverine) do not form cyclic compounds with nickel, cobalt, or copper (198, 253, 262, 284, 199). Pfeiffer has more recently found (199) that decamethylenediamine,  $\text{H}_2\text{N}(\text{CH}_2)_{10}\text{NH}_2$ , and octadecamethylenediamine,  $\text{H}_2\text{N}(\text{CH}_2)_{18}\text{NH}_2$ , are incapable of forming ring structures with copper or nickel corresponding to

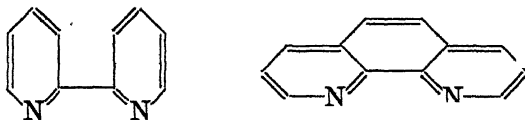


which would contain thirteen and twenty-one members, respectively.

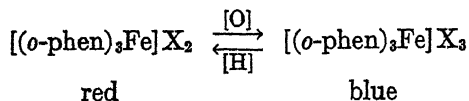
The metallic complexes of *o*-phenylenediamine,  $\text{C}_6\text{H}_4(\text{NH}_2)_2$ , are not as stable as those of the aliphatic amines (105).

b. Two  $\text{>N<}$  groups (both coördinating)

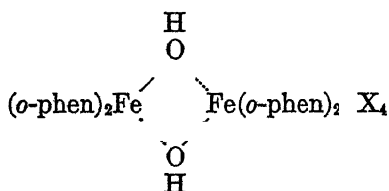
The very interesting metallic compounds with  $\alpha, \alpha'$ -dipyridyl and with *o*-phenanthroline



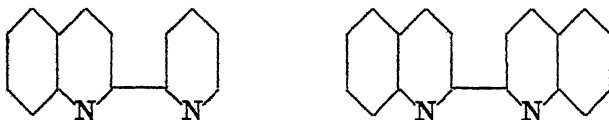
were discovered by Blau (20) in 1898. Among the numerous metallic derivatives of these compounds are the striking blood-red ferrous salts in which three molecules of the base are attached to one atom of iron,  $[\text{Fe}(\text{dipy})_3]\text{X}_2$  and  $[\text{Fe}(\text{o-phen})_3]\text{X}_2$ . The complex radicals are readily formed and very stable. They furnish an extremely sensitive test for ferrous iron (76, 229). On oxidation these red ferrous compounds are converted to blue ferric compounds, the shift in color being reversible. The *o*-phenanthroline complex was employed by Walden, Hammett, and Chapman (268) as an oxidation-reduction indicator and its utility has been rapidly extended (37). The shift



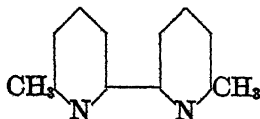
occurs at the high potential of 1.14 volts and is ideal for use in dichromate or ceric sulfate oxidation. While the *o*-phenanthroline ferric complex is readily produced by the oxidation of the ferrous complex as indicated above, the action of *o*-phenanthroline on ferric salts yields an amorphous brown powder (20), which has recently been shown by Gaines, Hammett, and Walden (86) to be a binuclear compound of the composition



The similarity in structure of  $\alpha, \alpha'$ -dipyridyl and *o*-phenanthroline immediately suggests that the condition for complex formation is simply that the cyclic nitrogen atoms be attached to adjacent carbon atoms. The isomeric phenanthrolines and  $\alpha, \beta'$ -,  $\beta, \beta'$ -, and  $\gamma, \gamma'$ -dipyridyl fail to give any reaction with ferrous iron. Much more surprising, however, was the discovery by Smirnof (239) that  $\alpha$ -pyridyl- $\alpha'$ -quinoline and  $\alpha, \alpha'$ -di-quinolyl

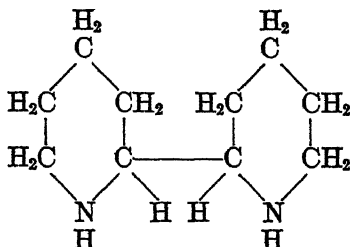


fail to give the ferrous reaction. Smirnof attributed this to a saturation of the residual affinity of the nitrogen atoms by the neighboring "aliphatic-like" conjugated double bond system of the benzenoid ring of quinoline. Willink and Wibaut (290) have found, however, that the test also fails with 6,6'-dimethyl-2,2'-dipyridyl.



Apparently the  $\alpha, \alpha'$ -linkage is a necessary but not the sole condition for chelation of these compounds. Smirnof predicted that the isomeric

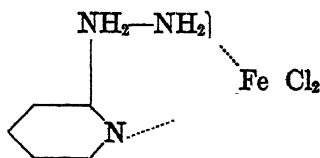
diisoquinolines joined by carbon atoms neighboring the nitrogen atoms will give the iron reaction, but this point has apparently not yet been tested.  $\alpha, \alpha'$ -Dipiperidyl



also yields a red ferrous complex (20).

c. One  $\text{>N/}$  group and one  $\text{—NH}_2$  group (both coördinating)

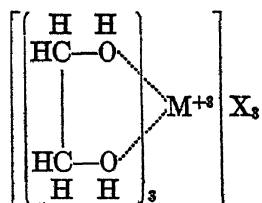
Somewhat similar to the ferrous dipyridyl compound is the ferrous complex with  $\alpha$ -pyridylhydrazine



described by Emmert and Schneider (62).

d. Two  $\text{—OH}$  groups (both coördinating)

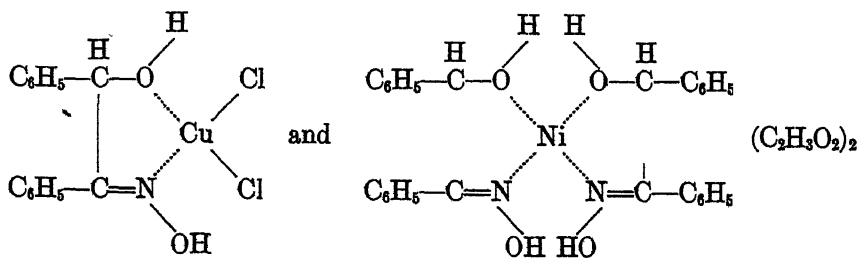
A great number of compounds were prepared by Grün and his co-workers (91, 92) in which ethylene glycol and several other 1,2-glycols, propyleneglycol, pinacol, etc., were coördinated to metals. Three molecules of the glycol but never more entered the compounds, corresponding to ring formation of the type:



Glycerol acts in a similar manner (93), but as three molecules always enter into the complex probably only two hydroxyl groups are coördinated, the third being left free, that is, glycerol functions as a bidentate rather than a tridentate molecule. Well-defined crystalline compounds have been obtained in these cases. Other less definite evidence along this line has also been presented (87).

e. One  $\text{—OH}$  group and one  $\text{=NOH}$  group (both coördinating)

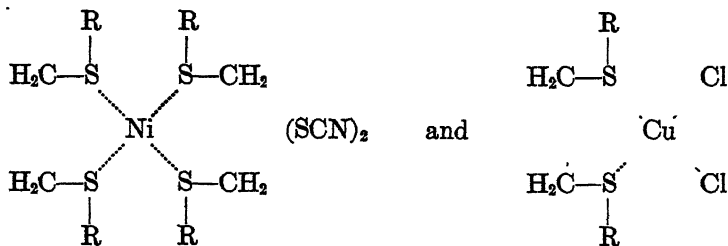
As mentioned previously,  $\alpha$ -benzoin oxime functions as a bidentate molecule in all three classes: i.e., both groups functioning as acids (B1, i); one as an acid, one by coördination (B2, l); and both by coördination. The latter case was observed by Jennings, Sharratt, and Wardlaw (144), who prepared the copper and nickel compounds



f. Two groups (both coördinating)

The organic monosulfides,  $\text{R—S—R}$ , form stable coördination compounds with a number of heavy metals, for example, platinum, palladium, and mercury. The copper and nickel compounds with the monosulfides are little stable or non-existent. With those disulfides where ring formation may occur, the stability is enormously increased and the copper and nickel compounds are well defined.

Tschugaeff (258, 265, 260, 267) studied a series of dithioethers of the general formula  $\text{RS}(\text{CH}_2)_n\text{SR}$ . Variation in the alkyl groups had little effect, although the aryl compound,  $\text{C}_6\text{H}_5\text{S}(\text{CH}_2)_2\text{SC}_6\text{H}_5$ , would not coördinate with copper or nickel. When  $n = 2$ , corresponding to the formation of five-membered rings by chelation, the disulfides gave fine crystalline compounds with nickel and copper of the type of

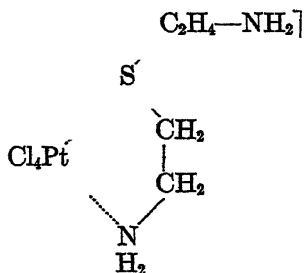


When  $n = 0, 1, 3$ , or  $5$ , corresponding to three-, four-, six-, or eight-membered rings, the ability to form metallic compounds was completely absent.

Morgan (182) has reviewed the chelate compounds of the dithioethers; surveying the periodic table systematically he concluded in general that the thioethers chelate with those metals which normally form sulfides. He has also measured the heats of formation of these compounds (180). The metallic derivatives of numerous other disulfides of this same type have been studied (14).

g. One  $-\text{S}-$  group and one  $-\text{NH}_2$  group (both coördinating)

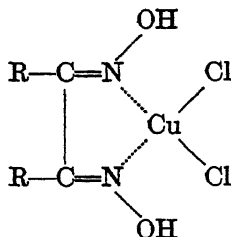
Mann (155) prepared a quadrivalent platinum compound with  $\beta, \beta'$ -diaminodiethyl sulfide, having the composition



The free amino group of this compound is capable of adding acids. By fractionally crystallizing the *d*-camphorsulfonate of this compound Mann isolated optically active components of the compound. The asymmetry of the molecule resides in the sulfur atom, which through coördination becomes similar in structure to the sulfoxides which had previously been resolved.

h. Two  $=\text{NOH}$  groups (both coordinating)

In their usual reactions the dioximes of the 1,2-diketones form chelate rings by the replacement of the hydrogen atom of one oxime group, the second oxime group attaching to the metal by secondary valence. The dioximes have also been found to form chelate rings by secondary valences alone (43, 235), giving copper compounds of the type



### C. THE TRIDENTATE COMPOUNDS

Of the four possible classes of tridentate compounds corresponding to the combinations of primary and coordinating valence, members of all classes are known, although the evidence in the case of class C1 is rather weak. The total number of tridentate compounds is very small.

#### C1. Three primary valences

Of the various tribasic acids which might enter into complex formation as tridentate groups, occupying three coordination positions about a metal atom, phosphoric acid is the first which is called to mind.

A number of salts of two phosphatoferric acids,  $H_2[Fe(PO_4)_2]$  and  $H_3[Fe(PO_4)_3]$ , were described by Weinland and Ensgraber (276). In the former the phosphate radical apparently occupies three coordination positions. The situation is very complicated, however. Jensen (115) has recently reviewed and extended some of the knowledge of these compounds.

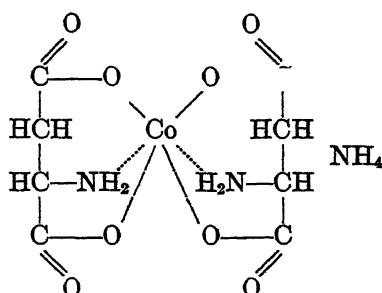
The action of phosphoric and citric acids on aquopentammino-cobalt salts leads to pentammino compounds in which only one limb of the acid occupies a coordination position (56).

#### C2. Two primary valences

##### a. Two $-COOH$ groups (acidic) and one $-NH_2$ group (coordinating)

That aspartic acid,  $HOOCCH_2CHNH_2COOH$ , and trivalent cobalt form a permanganate-colored lake was briefly noted by Lifschitz (147). Further investigation (289) of this phenomenon has shown that this deep permanganate-colored compound forms by the action of aspartic acid on cobaltic oxide or various cobalt amines; it is stable toward acids but sensitive to alkalis. The compound is very soluble in water, and evaporation of the solution yields only a glassy resin. Addition of ethyl alcohol or higher alcohols to its aqueous solutions gives only oily emulsions; methyl alcohol, however, precipitates a light lavender powder which is either the free acid  $H[Co(C_4H_5O_4N)_2]$  or its ammonium salt, depending on whether the compound was prepared from cobaltic oxide or a cobalt ammine. Although somewhat variable in composition, the ammonium salt was shown by conductivity measurements to be a uni-univalent electrolyte. Migration

experiments in agar gel indicate that the colored ion is negatively charged. The structure given the compound (289) is



Pfeiffer (202) has recently examined the copper derivative of aspartic acid and found it to be the cupric salt of copper aspartic acid,



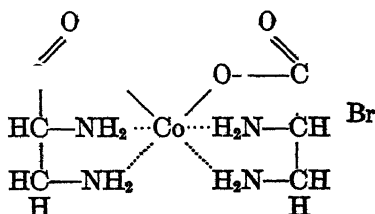
He prepared also the sodium and barium salts of the complex acid. Although Pfeiffer formulates the compound as having the aspartic acid molecules linked to the copper atom through the amino group and only one carboxyl group, leaving the second carboxyl group free, this is probably incorrect, and the complex diaspartato-cupric anion is better formulated like the above cobalt compound, that is, as a tridentate molecule.

Glutamic acid,  $\text{HOOCCH}_2\text{CH}_2\text{CHNH}_2\text{COOH}$ , forms copper compounds similar to those of aspartic acid (202). The lead (12, 122) and cobalt (236) derivatives are probably tridentate compounds of this class.

### C3. One primary and two coördinating valences

#### a. One $\text{—COOH}$ group (acidic) and two $\text{—NH}_2$ groups

The action of the  $\alpha,\beta$ -diaminopropionic acid hydrobromide on cobaltic oxide or, better, on carbonato-tetrammino-cobaltic bromide (289) leads to the complex cobalt compound  $[\text{Co}(\text{C}_3\text{H}_7\text{O}_2\text{N}_2)_2]\text{Br}$ . The salt crystallizes without water of crystallization, and conductivity measurements indicate that it is a uni-univalent electrolyte. The structure of the compound is undoubtedly

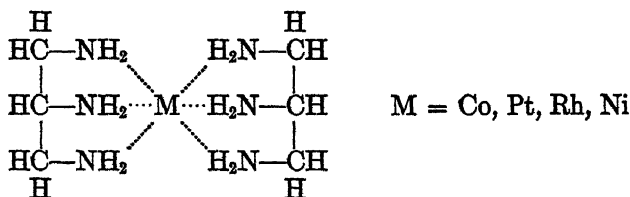




## C3. Three coördinating valences

a. Three  $\text{—NH}_2$  groups

A series of investigations into the coördination compounds of  $\alpha, \beta, \gamma$ -triaminopropane by Mann and Pope (162, 161) and later by Mann (151, 152, 153, 154, 156) has yielded unique and interesting results. With the metals of coördination number six, compounds of the general type

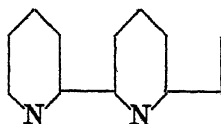


are produced in which one molecule of the triamine occupies three coördination positions about the metal atom. The great stability of these compounds is indicated by the fact that nickel and divalent platinum add two molecules of the triamine, forming compounds in which the coördination number is six; this is very unusual, at least in the case of the latter element.

The triamine can also act as a substituted diamine, the resulting complexes being of a very novel type.

b. Three  $\text{>N<}$  groups (coördinating)

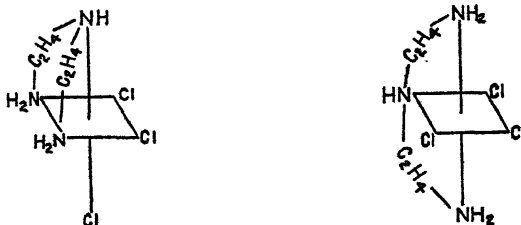
During the preparation of  $\alpha, \alpha'$ -dipyridyl by the catalytic dehydrogenation of pyridine, Morgan and Burstall (176) isolated  $\alpha, \alpha', \alpha''$ -tripyridyl,



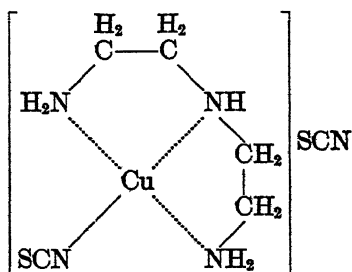
They found that this base gave a deep purple ferrous compound,  $[\text{Fe}(\text{tripyridyl})_2]\text{Br}_2 \cdot 1.5 \text{ H}_2\text{O}$ , in which the base apparently acts as a tridentate group. The platinum, rhenium, and rhodium complexes with the base were subsequently studied (177, 175). A method of determining iron in sea water has been devised (42) based on the reaction of the base with ferrous iron.

c. Two  $\text{—NH}_2$  groups and one  $\text{—N—}$  group (coördinating)

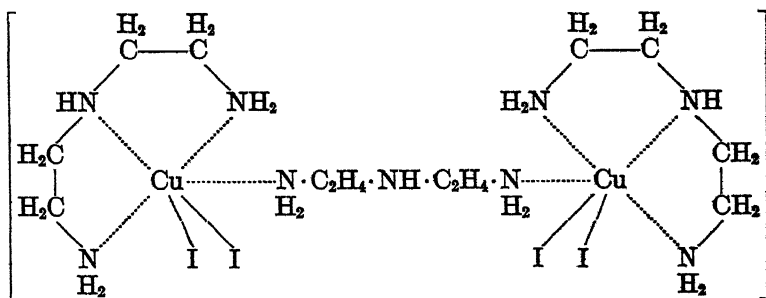
In an effort to prepare an optically active compound in which the asymmetry of the molecule was due to coördinated nitrogen, Mann (158) studied the coördination compounds of  $\beta, \beta'$ -diaminodiethylamine,  $\text{HN}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$ . Among other compounds he prepared several salts in which the amine functioned as a tridentate molecule. The platinum compound  $[\text{Cl}_3\text{Pt}(\text{diaminoethylamine})]\text{Cl}$  may have two configurations:



Only one form of the compound was obtained, however. A cobalt compound of the hexammine type was prepared,  $[\text{Co}(\text{diaminodiethylamine})_2]\text{I}_3$ , and two copper compounds:



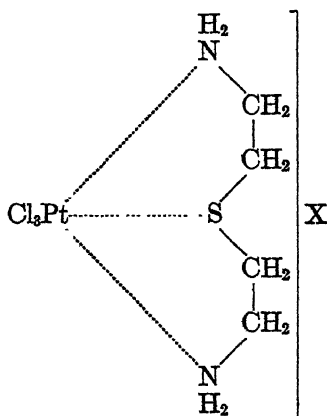
and



Peacock has also worked on similar compounds (190).

d. Two  $\text{—NH}_2$  groups and one  $\text{—S—}$  group (coördinating)

During a study of the stereochemistry of coördinated sulfur, Mann (155) obtained a tridentate platinum compound containing  $\beta, \beta'$ -diamino-diethyl sulfide



Two forms of this compound are possible, similar to those suggested above for the platinum salts of  $\beta, \beta'$ -diaminodiethylamine, but only one form was found.

## D. THE QUADRIDENTATE COMPOUNDS

*D1. Four primary valences*

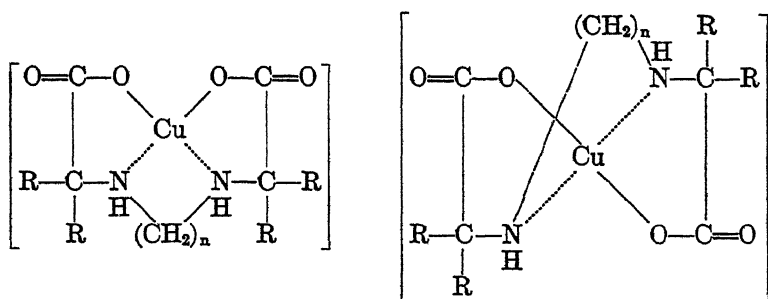
No examples of this class are known.

*D2. Three primary valences, one secondary valence*

No examples of this class are known.

*D3. Two primary valences, two secondary valences*a. Two  $\text{—COOH}$  groups and two  $\text{—NH}$  groups

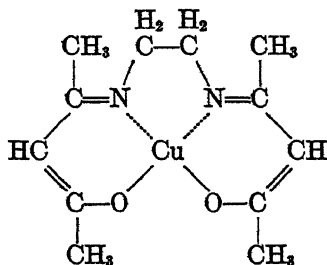
N. Schlesinger (234) investigated the copper salts of a number of polymethylene-bis-( $\alpha$ -imino acids) of the general formula:  $(\text{CH}_2)_n\text{—}(\text{NHCR}'\text{R}'\text{COOH})_2$ . For values of  $n$  of 2 and 3 a single form of the copper salt was found, blue in color; for  $n = 10$ , violet-colored salts resulted, but again only one form. For intermediate values of  $n$ , 5 and 7, two modifications, blue and violet, were obtained. The compounds were non-electrolytes, as indicated by conductivity measurements, and had normal molecular weights. Schlesinger attributed the existence of two forms of the intermediate members to *cis-trans* isomerism:



The spanning of the *trans*-positions of the copper atom can occur only with large values of  $n$ . Four different amino acids were tried in these compounds, and the results appear to be fairly general. The interpretation of these results has been criticized by Reihlen (210).

b. Two  $\text{—OH}$  groups (acidic) and two  $\text{=N—}$  groups (coördinating)

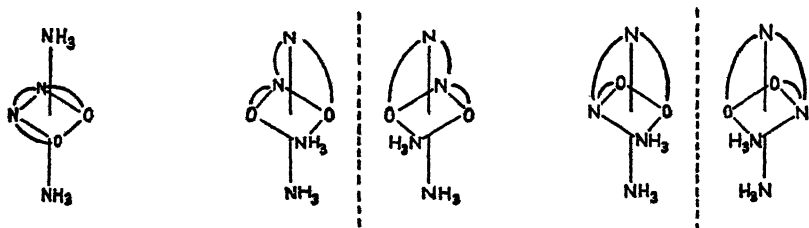
While trying to prepare a copper compound containing both ethylenediamine and acetylacetone, Morgan and J. D. Main Smith (186, 187) obtained a green copper salt of a condensation product of ethylenediamine with two molecules of acetylacetone. The copper compound, which has the following structure



had been obtained earlier by Combes in 1889.

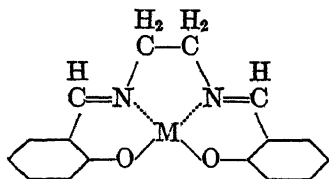
Beside furnishing copper, nickel, and palladium compounds which have all the properties of inner complex compounds (the nickel compound can be boiled without decomposition), the quadridentate behavior of the condensation product, ethylenediamine-bisacetylacetone (abbreviated as "ec"), was convincingly demonstrated by the preparation of the cobaltic compound,  $[\text{Co}(\text{NH}_3)_2\text{ec}]\text{X}$ . This compound exists in five forms,—one inactive form and two enantiomeric pairs,—all of which were found by Morgan and Main Smith. These forms correspond to the various pos-

sible arrangements of the quadridentate molecule about the coordination sphere:

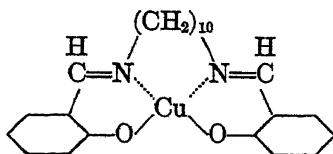


Both of the racemic mixtures were resolved and their optical rotatory powers found to differ considerably. These results are not only an example of excellent experimental work but a brilliant confirmation of the general principles underlying the formation of chelate rings.

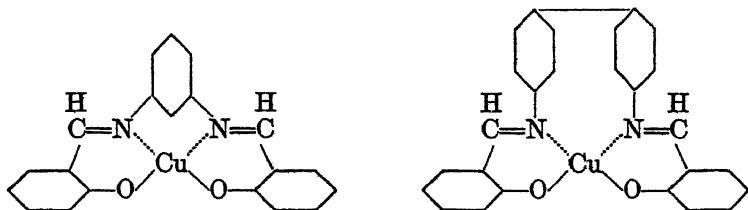
The formation of metal compounds with salicylaldehyde (B2, m) led Dubský and Sokol (53) to the metal salts of the condensation product of salicylaldehyde with a diamine. A condensation product of ethylenediamine with two molecules of salicylaldehyde was readily obtained by warming a mixture of their alcoholic solutions. This material gave inner complex nickel and copper compounds having the composition



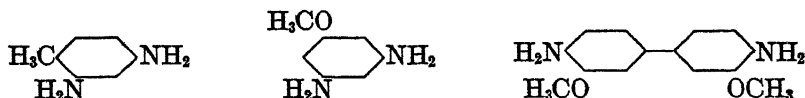
Pfeiffer greatly extended the field (194, 200) by using decamethylenediamine and various aromatic diamines in place of ethylenediamine. Like the derivative from ethylenediamine, the *o*-phenylenediamine compound yields metal compounds involving two six-membered and one five-membered ring. A thirteen-membered ring must be present, however, in



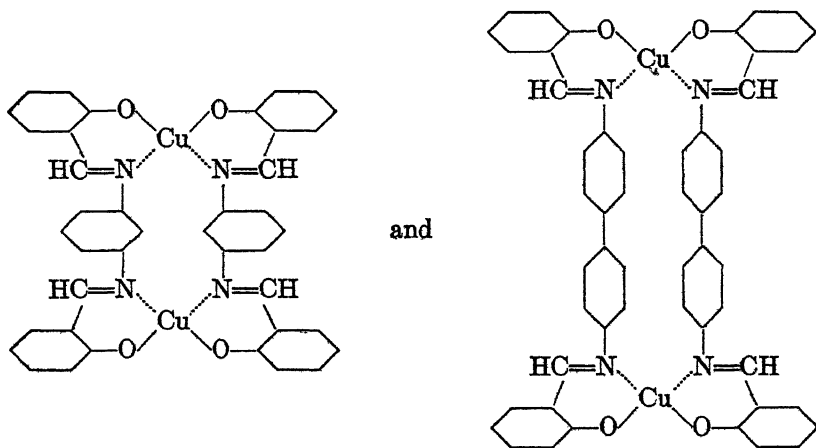
Very surprising is the fact that *m*-phenylenediamine and benzidine yield the same type of compound. On stereochemical grounds it seemed highly unlikely that these compounds would have the structures



While the molecular weights of the salts of the compounds derived from *o*-phenylenediamine and decamethylenediamine were shown to be normal, such evidence could not be obtained with the *m*-phenylenediamine and benzidine compounds because of their insolubility in all solvents. By using the following substituted diamines



analogous metal salts were obtained which were soluble in chloroform. Their molecular weights are double those of the simple formulas and Pfeiffer considers their structures to be

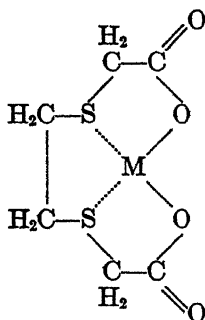


The corresponding *p*-phenylenediamine behaves in the same way, and again the copper derivative is too insoluble for molecular weight determina-

tions; the 1,4-naphthalenediamine compound is bimolecular, however, as well as the 1,5- and 2,7-naphthalenediamine derivatives, and probably the structures of these compounds are the same as those of the *m*-phenylenediamine and the benzidine derivatives.

c. Two  $\text{—COOH}$  groups (acidic) and two  $\text{—S—}$  groups (coördinating)

Probably the first synthetic quadridentate compounds recognized as such were the copper and bivalent platinum compounds of ethylene-bisthioglycolic acid of Ramberg and Tiberg (208)

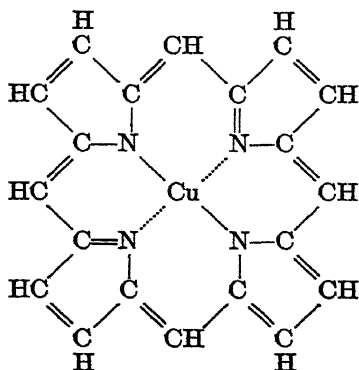


These were immediately known to be inner complex compounds because of their composition, saturated character, and insolubility in water. Similar compounds are prepared from propylenebisthioglycolic acid (212).

d. Two  $\text{—NH}$  groups (acidic) and two  $\text{>N<}$  groups (coördinating)

In this group fall the exceedingly important natural pigments, chlorophyll, the green coloring matter of the leaves, containing magnesium, and hemoglobin, the red pigment of the blood, containing iron. The classical work of Willstätter and of H. Fischer has given us an insight into the composition and structure of these materials. In both there is present the great porphyrin ring containing four pyrrole nuclei joined together through their  $\alpha$ -positions by methylene groups. The metals appear to be united to the nitrogen atoms of all four pyrrole groups, two by primary and two by secondary valences. In the case of chlorophyll the alcohol phytol, and in the case of hemoglobin the protein globin, is joined to the metal porphyrin molecule.

The parent unsubstituted porphyrin ring has been synthesized by Fischer (82). Its copper compound has the structure

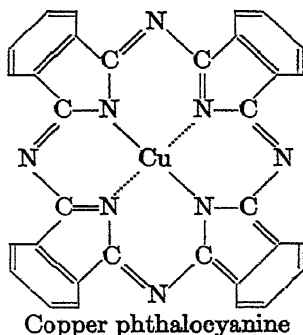
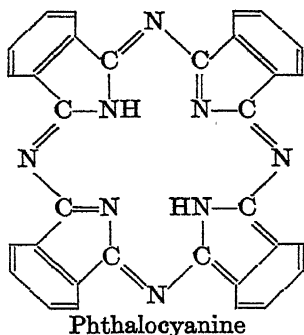


The porphyrins vary from this by substituents on the  $\beta$ -carbon atoms of the pyrrole nuclei.

The metal atom undoubtedly plays a significant rôle in the biological processes in which the natural pigments perform such essential functions, that is, the reduction of carbon dioxide by the plant and the transmission of oxygen by the blood, but our knowledge of how this occurs is still in a formative state (96, 224).

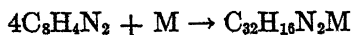
It is interesting to note that the oxygen carriers in the blood of various invertebrates contain copper, manganese, or vanadium (all metals of variable valence) instead of iron. The pinion feathers of the turacos, a species of tropical birds, contain a red pigment which is a copper porphyrin of structure similar to that given above (83).

In a very brilliant series of investigations the English chemist Linstead and his students (148) have very thoroughly investigated the blue by-product produced in the commercial manufacture of phthalimide by the action of ammonia gas on fused phthalic anhydride in iron vessels. To this deep blue substance they gave the name "phthalocyanine" because of its origin and color. The by-product material contains iron, but the free organic substance, also deep blue in color, has been isolated and shown to be a large cyclic molecule, markedly resembling the porphyrin rings, but composed of four phthalimide residues fused together through nitrogen atoms, forming a great ring of eight carbon and eight nitrogen atoms.





As in the porphyrins, metal atoms can be introduced into the center of the molecule, two hydrogen atoms being simultaneously displaced and the metal also coördinating with the other two central nitrogen atoms. Some twenty metallic derivatives have been prepared, including metals from each group of the periodic table. While these metallic derivatives can be prepared by the action of free phthalocyanine on the metals or their salts, the best way appears to be by the action of the metal on phthalonitrile, condensation and complex formation occurring simultaneously,



there being a great tendency for this to occur and the reaction being exothermal. The metallic products are of extraordinary stability, the copper compound, for example, subliming undecomposed at 580°C. In the case of bivalent metals the products have the formula  $\text{PcM}^{+2}$  ( $\text{Pc}$  = phthalocyanine minus 2 H); in the case of trivalent elements  $\text{PcM}^{+3}\text{X}$  ( $\text{X}$  being a univalent negative radical).

Detailed x-ray studies of the free phthalocyanine molecule and its metallic derivatives by Robertson (222, 223) have led to fruitful and very unique results, wholly in agreement with conclusions drawn by Linstead from chemical reasoning. As expected, the molecule is completely planar and the introduction of most metal atoms does not change the cell dimensions appreciably. The stereochemical implications of these compounds have been treated in a joint paper of Linstead and Robertson (149). An investigation into the magnetochemistry of the materials has also been made (123). It has been reported that metallic phthalocyanines are now being manufactured on large-scale production for use as pigments.

Linstead has also extended the study to the corresponding naphthalene compounds (32). Of the ten isomeric dicyanonaphthalenes only the 1,2- and 2,3- compounds undergo reaction with metals. From 1,2-dicyanonaphthalene and magnesium was obtained a mixture of isomeric forms corresponding probably to the four possible arrangements which the extra naphthalene rings may take up around the molecule.

#### *D4. One primary valence and three secondary valences*

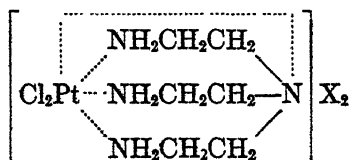
No examples of this group are known.

#### *D5. Four coördinating valences*

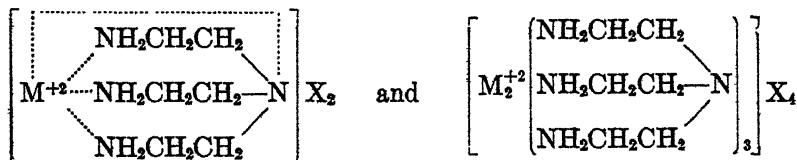
- |
- a. Three  $\text{—NH}_2$  groups and one  $\text{—N—}$  group (all coördinating)

Ordinarily the tertiary nitrogen atom is unable to form stable coördination bonds with metal atoms. In the coördination compounds of  $\beta, \beta', \beta''$ -

(triaminotriethyl)amine, studied by Mann and Pope (159), the coördination of the amino groups holds the tertiary nitrogen in the molecule, forcing it to coördinate. These are the first compounds of tetramines to be described, and apparently the first where an aliphatic tertiary nitrogen atom occupies a coördination position. With tetravalent platinum the base yielded the compound



with divalent platinum, nickel, and palladium the following compounds:



The arrangement of the four nitrogen atoms about a metal of coördination number four is difficult to picture sterically. Molecular weight and conductivity measurements indicate that the compounds are monomolecular. Reihlen (210) interpreted these compounds as proof of the tetrahedral distribution of the valences of the quadricovalent platinum atom,—the only distribution possible under the circumstances. The proof of the planar structure of the quadricovalent elements platinum, palladium, and nickel is now so overwhelming that the tetrahedral configuration is undoubtedly wrong. And yet the difficulty with the structure of these compounds still remains, as it is certainly impossible for the molecule to occupy the four corners of a square around the metal atom.

The corresponding triaminotripropylamine yields an analogous nickel compound, but not a platinum compound (160). Triaminotrimethylamine is apparently incapable of existence (121).

#### POLYDENTATE MOLECULES OF UNKNOWN CONSTITUTION

The ability of the peptides to dissolve freshly precipitated copper oxide was noted frequently by Emil Fischer (79) during the course of his researches on the amino acids and proteins. Although he remarked on the beauty and finely crystalline character of the copper derivatives, he analyzed relatively few and in no case attempted an explanation of their structure.

Structural formulas were assigned by Kober (126, 125) to the copper derivatives of the polypeptides; the reasoning underlying these formulations is often difficult to follow and the work needs further substantiation. Rising (218) and Wenaas (281) have also worked on these compounds. However, the field cannot yet be considered as settled.

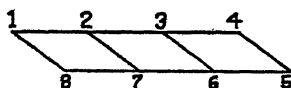
According to Fischer (81) the  $\alpha$ - and the  $\beta$ -amino acids are able to form copper salts, but the  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -amino acids are unable to do so. This is in accord with the work of Ley and Tschugaeff, as we have already seen (B2, a). The presence of a hydroxyl group in the molecule does not void this rule, as is shown by serine ( $\alpha$ -amino- $\beta$ -hydroxypropionic acid), isoserine ( $\alpha$ -hydroxy- $\beta$ -aminopropionic acid),  $\delta$ -amino- $\alpha$ -hydroxyvaleric acid, and  $\epsilon$ -amino- $\alpha$ -hydroxycaproic acid. Fischer pointed out, however, that the presence of more than one hydroxyl group might alter the situation.

Traube and W. Fischer (247) found this to be true, as copper hydroxide dissolved in  $\delta$ -amino- $\alpha$ , $\gamma$ -dihydroxyvaleric acid,  $\text{CH}_2(\text{NH}_2)\text{CH}(\text{OH})\text{-CH}_2\text{CH}(\text{OH})\text{COOH}$ , giving a complex compound which could be isolated only as a dark blue glass but which had the constant composition  $\text{Cu}_3(\text{C}_5\text{H}_8\text{O}_4\text{N})_2 \cdot 8\text{H}_2\text{O}$ .

The same curious relation of two atoms of copper to three molecules of hydroxyamino acid exists in the copper salt of hydroxyaspartic acid,  $\text{HOOCCH}(\text{NH}_2)\text{CH}(\text{OH})\text{COOH}$ , prepared by Dakin (46),



It will be noted that if the four valences of the copper atom lie in one plane and the -ol type of polynuclear linkage be present that a trinuclear molecule will afford just the eight coordination positions required by the eight active groups of the two molecules of amino acid.



Considerable work will have to be done before such a configuration can be regarded as established.

Analytical data appear to point toward a tridentate structure for the copper salt of isoserine (80).

The combination of metals with proteins has also been attacked from other angles (240, 188).

The activation of the enzyme arginase by metals has been pointed out by Hellerman (97), who believes that complex formation of some sort occurs between the metal and the enzyme. If so, the product is probably polydentate in character.

## THE EVIDENCE FOR CHELATION

The chelate rings were a natural outgrowth of the coördination theory. Just when a cyclic structure was first proposed for one of these compounds is difficult to determine. The idea of ring structure in the ethylenediamine complexes runs subconsciously through the early papers of Werner without being definitely expressed. In 1901, however, Werner (283) specifically assigned a cyclic structure to platinum acetylacetonate, and other similar structures were soon suggested: for copper glycine by Ley (134), for nickel dimethylglyoxime by Tschugaeff (262), and so on.

A great body of consistent evidence has been built up proving the existence of the chelate rings, and while the principles stated or assumed in the foregoing work can hardly be doubted, the underlying facts should not be forgotten. Briefly they are these:

1. While the coördination number of certain metals is invariably four or six in thousands of cases of unidentate compounds, only two or three molecules of organic compounds bearing two associating units unite with such metals. Providing the compound be monomolecular, attachment of all four or six units with subsequent ring formation must be assumed if the coördination positions are to be all occupied.

2. The failure of analytical tests for the metals on solutions of their complex salts shows the absence of the simple ions of the metal, and conductivity and migration experiments prove the complex ion to be a non-electrolyte, anion or cation, as calculated assuming chelation to occur.

3. The compounds are saturated and incapable of adding further coördinating addenda; for example, copper glycine will not take up ammonia (134).

4. Absorption spectra curves are identical with analogous compounds known not to be cyclic (133, 138).

5. Predictable isomeric phenomena have been realized, as for example with the glycine compounds of cobalt and platinum and the dioximes of nickel and palladium.

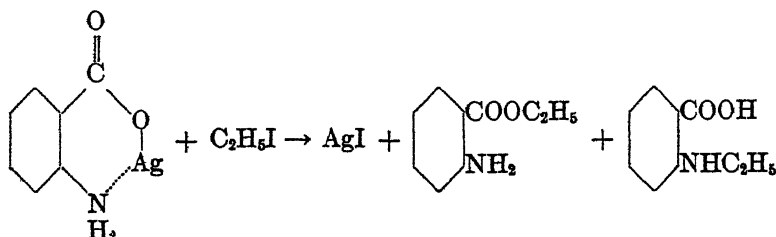
6. Compounds rendered asymmetric by chelation have been resolved in numerous cases.

7. Groups involved in chelation are non-reactive, such as the carbonyl group of the acetylacetonates, which will not react with phenylhydrazine (211, 63), the amino group of the amino acid salts, which cannot be acetylated (122), and so on.

8. The formation of the chelate type of compound occurs only with those organic molecules which are stereochemically so arranged as to yield rings of four to seven members and not by those not so arranged, this difference generally being very sharp.

9. Chelating groups enter equally into reactions when a chelate ring is

broken by double decomposition, as shown by Karrer (120) in the reaction of the silver salt of anthranilic acid with ethyl iodide:



Taken together these facts are abundant proof of the cyclic nature of the chelate compounds.

From the foregoing survey it will be readily appreciated that the chelate rings have an unusual application to a variety of otherwise unrelated fields.

The mechanism of the function of the metals in biochemical problems is known to be chelate in nature in the case of chlorophyll and hemoglobin, and undoubtedly the part played by metals in the activity of certain enzymes and in the nutritional requirements of the plants and animals is of the same character.

The great saving of time and the increased accuracy in analytical processes which result from the discovery of specific organic reagents is so obvious as to require little mention. The best reagents which have been proposed so far are of the non-electrolyte chelate *inner complex* type. Feigl, Berg, and other workers have been pursuing this field for some time, and their results are most encouraging.

In furnishing a neat and comprehensive theoretical basis for mordant dyeing Werner and, later, Morgan and his students have made an exceptionally valuable application of the chelate rings.

For settling the questions related to the stereochemistry of the metals the chelate rings have proven a very useful and fruitful tool, and further examples of this are appearing regularly. In the field of organic chemistry the chelate compounds have been employed in deciding questions of structure and in following changes in configuration. Many pharmaceutical preparations are chelate compounds.

In the chelate compounds, therefore, we have a field of widely different and important applications, a field which combines all the attraction of synthetic chemistry and stereochemistry with the possibilities of solving important problems in analytical and biochemistry. It is a field, however, which has many uncharted regions and offers abundant opportunity for exploration.

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# THE COMPLEX COMPOUND THEORY OF COLLOIDAL OXIDES

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## INTRODUCTION

The term "colloidal oxide" needs some explanation because it is an inexact expression. It refers to those colloidal dispersions which are produced by the hydrolysis of a metallic salt or by the peptization of the hydrous oxide of a metal. These are not truly dispersions of the oxide, because it has been shown by numerous investigators that a stable hydrosol cannot be produced without the presence of ions other than those of the metal and hydroxyl and hydrogen. Thus Thomas and Frieden (23) showed that so-called ferric oxide hydrosols always contain the anion of the ferric salt from which they were precipitated. The same thing is true for the hydrosols of aluminum, beryllium, chromium, gold, platinum, silver, and tin. Sorum (19) is unique in claiming to have prepared a colloidal dispersion of pure ferric oxide. Since the preponderance of evidence points to a complex dispersed phase in the so-called metallic oxide hydrosols, an attempt is made in this paper to present a theory concerning the structure of the micelles which is more in accord with observed facts. Although this theory may have more general applications in the field of colloid chemistry, no attempt is made here to extend the theory beyond the experimental facts upon which it is based.

Much controversy has arisen over the structure of these colloidal oxides and the cause of their stability in aqueous media. This may be due to the fact that the composition of the dispersed phase is not such that it can be represented by a simple formula. This was pointed out also for crystalloid oxides by van Bemmelen (32) as early as 1888. Furthermore, it has been shown repeatedly that the properties and composition of colloidal oxides depend upon the experimental conditions under which the oxides are prepared. The concentration of the metallic salt, the manner of preparation, the temperature of preparation, the anion of the metallic salt, and the age of the hydrosol are all important factors in determining the composition and properties of the hydrosol. These facts have led many investigators to conclude that the dispersed phase is not a true

compound, since its composition is so easily varied. Those investigators who do not think of the colloidal oxide as a compound have applied descriptive terms which are equally vague. Thus hydrosols which are readily precipitated by electrolytes are called *hydrophobic*, while those that are difficult to precipitate with electrolytes are called *hydrophilic*. This would indicate two distinct classes of colloids, but there are many colloidal oxides which are intermediate in properties between the typical *hydrophobic* and the typical *hydrophilic* colloids. These terms are used in this paper in a relative sense only, to describe rather than to classify colloids.

#### SOME PREVIOUS THEORIES

The first important work in this field was done by Thomas Graham (6) in 1862, when he prepared the hydrous oxides and hydrosols of aluminum, chromium, iron, molybdenum, tin, titanium, and tungsten. From this time on investigators too numerous to list have prepared colloidal oxides and studied their properties.

The early studies on these systems indicated that the behavior of colloidal oxides differed markedly from that of most crystalloid solutions. The variation in freezing point, boiling point, osmotic pressure, and viscosity with increasing concentration was so different from the behavior of true solutions that many doubted if these colloidal dispersions followed the laws of physics and chemistry. Attempts to determine the molecular weight of the dispersed phase often gave values as high as 800 for the colloidal oxides and 100,000 for hydrophilic colloids like albumins dispersed in water. This led to the belief that no formula would express the composition of the dispersed phase, and so physical principles were used to explain them, rather than chemical principles.

It is therefore logical that the first theories concerning the stability of hydrosols were almost purely physical. One of the first theories was based upon the facts of electrostatic attraction and repulsion. Thus, if the dispersed particles were postulated to be charged particles of similar sign, then mutual repulsion would prevent their coagulation and settling out. The origin of this electric charge was assumed to be due to frictional forces within the sol. The precipitation of the colloid was explained as being due to the discharge of the electric charge on the particles. This theory had the advantage of being simple, but it was shown to be untenable by the now classic papers of Smoluchowski (18) and of Porter and Hedges (15).

Another approach to an electrical theory of stability was begun by Helmholtz (8), who postulated the existence of an electrical double layer around the dispersed particles. Helmholtz derived his theory from data on electrokinetic behavior of colloidal dispersions. According to this

theory each particle of the dispersed phase carries an electrical charge on its surface, and surrounding this is a layer of solution which has an equal and opposite electric charge, similar to the relation between the plates of a charged condenser. Naturally this sets up a potential difference; according to Helmholtz this electrical potential is responsible for the stability of the dispersion, and the reduction of this potential to zero will cause precipitation of the dispersed phase. The rigid nature of the Helmholtz double layer has been modified by Gouy (5) and by Debye and Hückel (4) to agree more closely with modern ionic theories. According to their modifications the electrical layer of the solution is more diffuse and decreases in strength as the distance from the particle increases.

Still another theory based upon electrical potential and osmotic force has been advanced by John Arthur Wilson (35). Wilson assumes that a dispersed particle is a rigid sphere which may become electrically charged by attracting to itself ions from the surrounding medium. Thus a charged layer of ions surrounds each particle. Wilson further assumes that the ions bound to the particles are balanced by ions of opposite charge in the solution, producing an electrical double layer. Now, assuming that the ions on the particles are not free to move while those in the solution are free to move, Wilson invokes the Donnan equilibrium and shows that there will be more mobile ions within the double layer than outside of it when equilibrium is established. As a result of this unequal concentration of mobile ions inside and outside the double layer a potential difference and osmotic pressure will be set up. Since this will happen around each particle there will be a repulsive force between them, and this will result in a stable dispersion. The addition of other electrolytes will upset this equilibrium, reduce the potential, and cause precipitation. Although Wilson derived his theory for a hydrophobic dispersion such as a gold sol prepared by the Bredig arc method, he applies it to hydrophilic colloids such as gelatin dispersed in water.

Finally there is the very popular theory of adsorption. This theory postulates that a dispersed particle may attach to itself either positive or negative ions according to the preference which the particles have for such ions. These ions are said to be adsorbed by the dispersed particles. Ions of equal and opposite charge remain in the dispersion medium and act as balancing or contra ions, thus keeping the solution as a whole electrically neutral. This theory is most convenient, since a particle may at one time prefer positive ions and at another time negative ions. It has been given wide publicity by Bancroft (1) and others. It does not differ essentially from the previous theories in explaining the stability and precipitation of colloids, since it postulates mutual repulsion of charged particles as the cause of stability and the neutralization of these charges as the cause of precipitation.



It will be noted that all of these theories have one common element in them and all have the same inherent weakness. If these theories are correct, then three facts should be consistently found experimentally. First, oppositely charged particles should mutually precipitate when added in equivalent amounts. Second, particles of the same electric sign should stabilize each other, or at least not precipitate each other. Third, no stable dispersion should be possible unless the dispersed particles are electrically charged.

To consider the first point mentioned above, the work of Schulze (16) may be cited. Schulze studied the effect of ions in precipitating arsenious sulfide hydrosol, and since the sol was negative he placed the emphasis on cations. Schulze thought that he discovered a consistent relation between the valence of cations and their precipitating power for negative sols. This rule, which is sometimes called Schulze's valence rule, states that if a power of 1 is assigned to monovalent ions, then divalent ions will have a power of 60, and trivalent ions a power of 1650. However, this rule has been discredited by such a variety of data that it is no longer taken seriously. One of the first to discredit it was Hofmeister (9), who demonstrated that the specific nature of the ion is often more significant than its charge, since ions of the same sign and valence may have widely different precipitating powers. Thus mere neutralization of charge is secondary to the specific nature of the precipitating ion. In addition to Hofmeister's work, Loeb (11) has demonstrated that in the case of hydrophilic colloids one may reduce the electrophoretic potential difference to zero and not cause precipitation of the dispersed phase. Thus the first point, that neutralization of electric charge is sufficient to produce precipitation, is very doubtful.

Now to consider the second point. There are numerous instances reported in the literature where hydrosols of the *same* sign will mutually precipitate when mixed. Thus Odén's sulfur sol, which is negative, precipitates arsenious sulfide hydrosol, which is also negative. Likewise Odén's sulfur sol precipitates Carey Lea's silver sol, which is negative. To cite one other case, negative vanadium pentoxide hydrosol precipitates negative uranyl oxide hydrosol (22). Thus it will be seen that similarly charged particles may mutually precipitate making the second point untenable and also reflecting on the first point, since precipitation occurred without neutralization of the electric charges on the particles.

Finally there are data on the third point. Several stable sols have been reported in which the dispersed phase was not electrically charged. Stable dispersions of proteins at their isoelectric point have been reported by Loeb (11). Dispersions of  $\beta$ -amylose (from starch) in water media are reported by Thomas (22) to be uncharged. Soyenkoff (20) has reported

the preparation of several metallic soap dispersions in benzene in which the dispersed particles had no electric charge.

From the data cited above it should be evident that electric charge is not the whole story concerning the formation, stability, and precipitation of colloids. There is such a wealth of facts which the electrical theories cannot explain and there is so much evidence pointing to the importance of the specific nature of each ion that they seem to be no longer tenable.

#### THE COMPLEX COMPOUND THEORY

All of the previous theories have centered their interest around stability and precipitation of sols with little attention to the structure of the micelles. The complex compound theory puts the interest on the structure of the micelle rather than on the cause of stability. There is no adequate explanation of why cane sugar or sodium chloride remains in solution in water. If simple crystalloidal solutions are not yet explained, how much chance is there to explain the stability of such complicated systems as many colloids are?

The complex compound theory attempts to relate colloidal behavior more closely to crystalloidal behavior, to explain the more recent experimental facts, and to provide a basis for predicting the behavior of systems similar to those for which the theory was derived.

There is ample evidence for the belief that true solutions and colloidal dispersions of the same material are different in degree only. The transition in properties from a true solution to a colloidal dispersion is gradual. Loeb (11) has shown this for hydrophilic colloids in his studies on the properties of true solutions of low molecular weight amino acids as compared with colloidal dispersions of high molecular weight amino acids and proteins. Whitehead and Clay (34) have shown the same thing for the transition in properties from a true solution of aluminum chloride through the more basic aluminum chlorides to the aluminum oxychloride hydrosol. Figure 1 shows the effect of adding sodium succinate to solutions of  $AlCl_3$ ,  $Al(OH)Cl_2$ ,  $Al(OH)_2Cl$ , and to the hydrosol. It will be noted that the change in pH value caused by addition of the salt is similar in all cases, increasing from the aluminum chloride to the hydrosol gradually. An explanation of this change will be given later in this paper. It is offered here merely to emphasize the close relation between solutions and hydrosols.

To explain how a solution of aluminum chloride can be gradually transformed into a hydrosol, the complex compound theory pictures a salt like aluminum chloride according to the Werner theory, which says that aluminum chloride is really  $[Al(H_2O)_6]Cl_3$  and that in solution there will be six water molecules coordinately bound to the central metallic ion

forming a complex ion, while the three chloride ions will be outside of this complex ion.

Since aluminum chloride is the salt of a strong acid and a weak base, it will hydrolyze when dissolved in water, giving an acid solution. Pfeif-

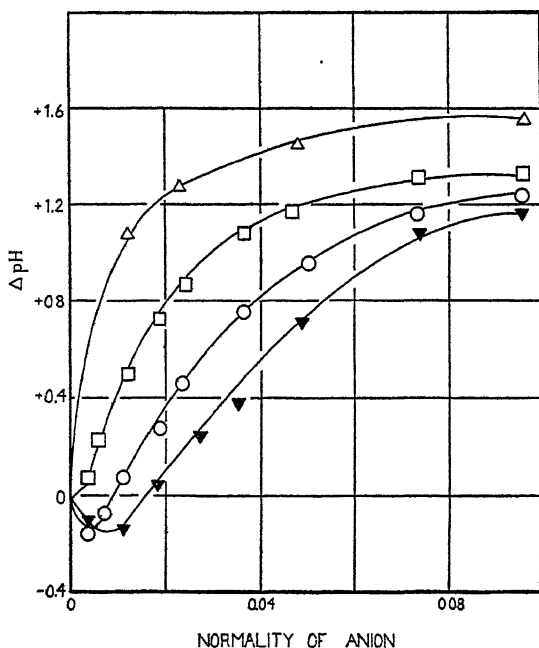
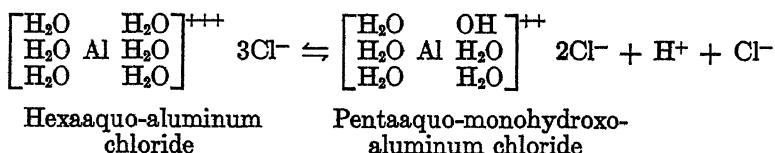


FIG. 1. Effect of sodium succinate on aluminum salts and sol.  $\Delta$ , sol;  $\square$ ,  $\text{Al}(\text{OH})_3\text{Cl}$ ;  $\circ$ ,  $\text{Al}(\text{OH})_2\text{Cl}_2$ ;  $\blacktriangledown$ ,  $\text{AlCl}_3$ .

fer (14) proposes that this hydrolysis be pictured in terms of the Werner structure as follows:



This process would produce an acid solution and a basic aluminum salt. The extent of the hydrolysis will of course be increased by a rise in temperature, as shown by Kulgren (10), by dilution, and by adding alkali to the solution. It is also dependent upon the anion of the salt, as shown by Čupr (3). However, alkali has the most pronounced effect on the



complex compound theory extends this process to include the formation of larger polynuclear complexes until colloidal dimensions are reached.

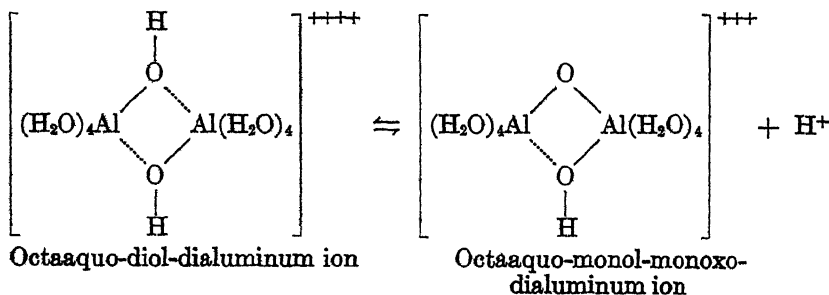
The above picture is the simplest possible one for a polynuclear complex, because anions of the salt would also be in some of the coördinate positions occupied by hydroxo or aquo groups in the above representation.

If this postulation is correct, then these polynuclear complex ions should act like other Werner complexes and there should be an equilibrium between the coördinately bound groups within the complex and the ions outside of the complex. Also, there should be an equilibrium between aquo groups within the complex and water molecules outside the complex. This would mean that any change in concentration of ions outside the complex would alter the equilibrium between complex ion and outer solution, resulting in a change of composition in the complex ion. It would also mean that a change in temperature would alter the equilibrium between aquo groups and water molecules, because increased temperatures usually cause aquo groups to move out of the complex. Finally, the composition of a complex ion formed in the solution might continually change until a stable equilibrium had been established between the complex ion and the solution outside of the complex. There is experimental evidence that all of the above conditions are fulfilled in various systems.

#### A. Evidence from heating

It was found by Thomas and Whitehead (30) that when an aluminum oxychloride hydrosol was obtained by peptizing hydrous alumina with hydrochloric acid at 20°C. and was then heated, the pH value of the sol decreased, i.e., it became more acidic. This might be ascribed at first thought to increased hydrolysis, because increased temperature usually increases the extent of hydrolysis, but in this case it was not a true hydrolysis because on cooling the sol back to 20°C. the pH did not return to its original value. Only after six weeks did the original pH value of the sol return.

This fact can be readily explained on the Werner-Pfeiffer basis. Assuming that the aluminum oxychloride sol was a polynuclear complex and taking the simplest complex to illustrate this point:



In the above case one of the ol groups lost a hydrogen ion to the outer solution and became an oxo group (oxygen bridge). This would increase the acidity of the outer solution and so decrease the pH value. Since the oxo group is less reactive than an ol group the equilibrium would not be restored at once upon cooling the system, but eventually the hydrogen ion would go back into the complex and change the oxo group back into an ol group. Both of these processes are indicated by the data plotted in figure 2, in which aluminum oxyiodide hydrosol is treated with potassium chloride and potassium sulfate before heating and after heating the sol. It will be noted that the two upper curves represent the effect of

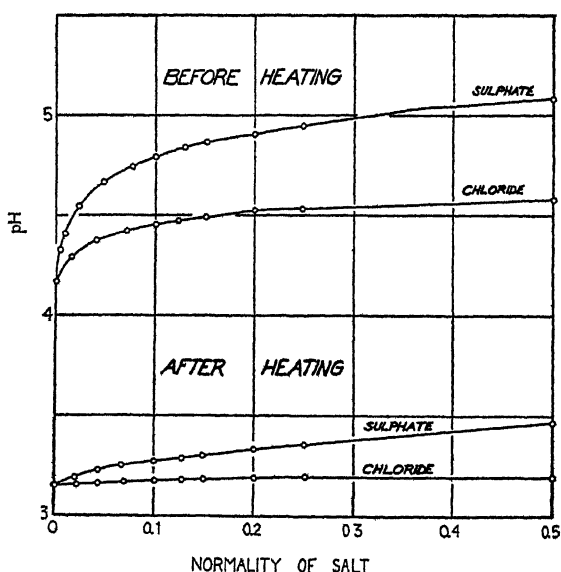


FIG. 2. Effect of potassium salts on pH of aluminum oxyiodide sols

salts upon the pH of the sol before heating. These curves begin at pH 4.17, while the lower curves representing the sol after heating begin at pH 3.15. Thus heating alone lowered the pH from 4.17 to 3.15. The explanation of this, as given above, is due to the changing of ol groups to oxo groups with a loss of one hydrogen ion per group from the inner complex to the outer solution. Thus the outer solution was made more acid. Again examining the curves, it will be noted that a given amount of salt caused a greater change in pH value in the upper curves than in the lower curves. This is interpreted as meaning that the oxo groups present in the sols represented in the lower curves were less reactive than the ol groups present in the sols represented in the upper curves. In other words,

the anions of the salts could more easily replace *ol* groups than they could *oxo* groups, and this is reflected in the relative change in pH values as plotted in this figure. The data are taken from the work of Thomas and Tai (27).

It will also be noted that oxolation decreases the charge on the complex ion, and so its speed of migration under the influence of an electric field should be decreased. This was found to be the case.

The data of Thomas and Tai given above are not isolated examples by any means. Similar results were obtained by others,—by Todd (31) for aluminum oxybromide sols, by Thomas and Whitehead (30) for aluminum oxychloride sols, by Thomas and von Wicklen (29) for chromium oxychloride sols, by Thomas and Kremer (24) for thorium oxychloride sols, and by Thomas and Miller (25) for beryllium oxychloride sols. In fact this behavior seems to be uniform for the so-called metallic oxide hydrosols, whether they are formed by hydrolysis or by peptization.

### *B. Evidence from aging*

All of the investigators cited above found that if metallic oxysalt hydrosols are prepared at room temperatures and allowed to age at room temperatures they become more acid, but if they are heated or prepared at elevated temperatures and then allowed to age at room temperatures they become more basic. The explanation of these facts on the complex compound basis is similar to that just given for the effect of heating alone. That is, when no heat is applied hydrolysis is the principal reaction taking place, and since the equilibrium of high molecular weight complexes with their outer solutions requires considerable time for completion, the hydrogen ion concentration of the outer solution gradually increases. But if heat is applied ololation occurs first, after hydrolysis, and then oxolation takes place, making the sol quite acid. Upon aging a reversal of these processes occurs and the outer solution becomes *less* acid.

### *C. Evidence from salt effects*

It has been known for decades that when a hydrous oxide is precipitated from a solution of one of its salts by the addition of an alkali, the precipitate invariably contains more or less of the anion of the salt. Thus hydrous ferric oxide precipitated from ferric acetate or ferric chloride always contains acetate or chloride ions which are very hard to remove (23). The presence of the anions has been accounted for by some chemists as impurities which are adsorbed or occluded. However, the complex compound theory explains them in another way.

Thomas and Whitehead (30) showed that when a neutral salt is added to aluminum oxychloride hydrosols, the pH value of the system increases.

This increased basicity is too great to be accounted for by ordinary physical chemical principles such as hydration of ions, salt effect on the quinhydrone electrode used to measure pH, or increased ionic environment. However, the Werner theory offers an explanation of the facts found. Werner postulated that the composition of a complex ion was not invariable, and that ions outside the coordinated complex might displace a coordinated group and take its place in the complex ion. It is well known that in crystalloidal complexes anions can replace aquo and hydroxo groups. Therefore the complex compound theory proposes that when a neutral salt is added to a metallic oxysalt hydrosol, the anion of the salt displaces hydroxo groups from the complex ion and forces them into the outer solution and makes that solution more basic. Čupr (3) demonstrated that the dissociation of a complex ion is a function of the anion

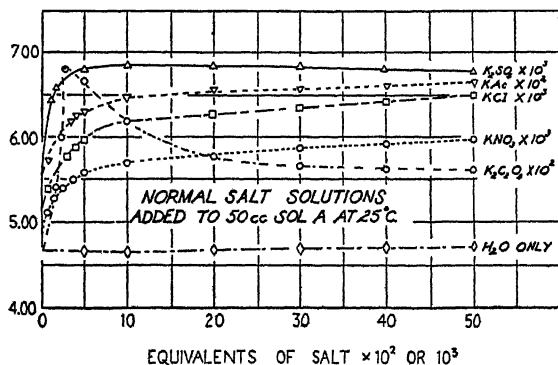


FIG. 3. Effect of salts on pH of aluminum oxychloride sol

present, and all anions are therefore not equal in their power to displace groups from the complex. This same conclusion was reached by Thomas and Whitehead (30) after studying a variety of salts. A typical set of data is plotted in figure 3. These data represent the effect of adding neutral salts to an aluminum oxychloride hydrosol. It will be noted that the effectiveness of the anions in raising the pH value of the sol was: oxalate > acetate > sulfate > chloride > nitrate. This is the same order which has been found for the stability of similar crystalloid complexes, such as cobaltammine complexes and chromic chloride complexes.

Similar results have been obtained for the hydrosols of beryllium (25), chromium (29), thorium (24), and zirconium (26).

If this complex compound theory is consistent, then there ought to be cases of hydrosols in which the cationic complex would be changed into an anionic complex just as crystalloidal complexes are. For example, it



is well known that the oxalate ion forms anionic complexes with many metal ions, a typical compound being  $K_3[Co(C_2O_4)_3]$ , potassium trioxalato-cobaltate. Thomas and Miller (25) treated beryllium oxychloride sols, in which the beryllium complex was a cation, with sodium or potassium oxalate and converted the beryllium complex into an anionic beryllate ion. Analysis of the new complex showed it to be a complex anion composed of beryllium ion, oxalato, aquo, and other coördinated groups. This colloidal beryllium complex thus acted exactly like crystalloidal complexes. Similar behavior was exhibited by the hydrosols of thorium (24) and zirconium (26).

Thus according to the complex compound theory the inclusion of anions in the hydrous oxide precipitate is more than a mere impurity,—the anion is part of the complex and can be removed from the complex only by replacing it. Of course washing will gradually do this by substituting aquo groups for the anion. If this concept is correct then nitrate ion should be most easily washed out, chloride next, then sulfate, and hardest of all oxalate, tartrate, or citrate. Such is the case.

#### *D.. Evidence from conductivity*

The data presented by figure 3 show the effect of neutral salts upon the pH of an aluminum oxychloride sol and were interpreted as representing the displacement of hydroxo groups by the anions of the added salt. There is supporting evidence for this belief in conductivity titrations performed by Miller (25) on beryllium oxychloride sols and soluble silver salt solutions. In these cases the concentration of silver salt was so low that the anion could not displace hydroxo groups but could displace the more easily displaced groups, chloro and aquo. Figure 4 shows the effect upon the conductivity of a beryllium oxychloride sol of adding silver nitrate, acetate, and tartrate.

It will be noted that the addition of the silver salt solutions first decreased the conductivity of the system to a minimum and then increased it. The explanation, according to the complex compound theory, is that the anions of the silver salts displaced chloro groups and possibly aquo groups from the complex. If chloro groups are displaced, then they will appear as chloride ions in the outer solution and be precipitated by silver ions. This would lower the conductivity of the system. Also, if aquo groups are displaced from the complex by anions, the net positive charge on the complex ion will be decreased and this would also decrease the conductivity. Once the displacement of chloro and aquo groups has ceased, the further addition of silver salt solutions will increase the conductivity of the system. It may be argued that no account is taken of relative ionic mobilities in the above explanation, but this variable has

been considered in detail for a large number of anions by Thomas (22), and the order of conductivity lowering and the order of anion mobilities are not the same. Therefore the conductivity data cannot be explained by differences in ion mobilities alone, but, using the mechanism outlined above and admitting the influence of ion mobility, an explanation results which is in accord with the facts.

### *E. Evidence from peptization*

If the complex compound theory is to be inclusive it must explain the formation of hydrosols by peptization as well as by hydrolysis. Thomas

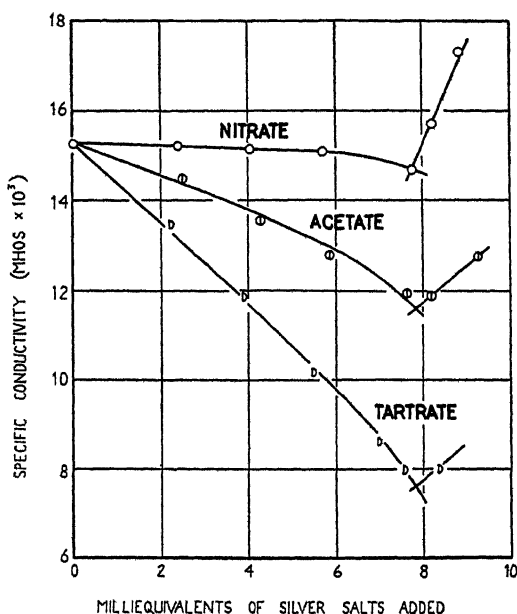


FIG. 4. Effect of silver salts on conductivity of beryllium oxychloride sol

and Vartanian (28) have studied the peptization of hydrous alumina by several acids. They found that equivalent amounts of acid were not equally effective in peptizing hydrous alumina. In fact, the effectiveness of an acid in peptizing hydrous alumina was inversely proportional to its tendency to form coordinate complexes with aluminum. Thus nitric acid is an excellent peptizing agent, while oxalic acid is very poor. It will be recalled that nitrate ion was very weak in forming complexes, as shown by its relatively small effect on the pH value of the aluminum oxychloride sols (figure 3) and in decreasing the conductivity of beryllium oxychloride sols (figure 4), while oxalate ion is very powerful in these respects. The

complex compound theory therefore explains peptization in the following way: A hydrous oxide contains many hydroxo groups and aquo groups coordinately bound to the central metallic ions; this complex is not soluble in water to any appreciable extent, but when an acid is added to it the hydrogen ions convert many hydroxo groups to aquo groups and ol groups to aquo groups, thus increasing the solubility of the complex in water. However, if the anion of the acid forms very stable coordinate complexes with the central metallic ion, then aquo and hydroxo groups will be displaced by the anion and a less soluble complex will be formed. Therefore those acids whose anions form highly dissociated complexes are best for peptization, while those acids whose anions form very slightly dissociated complexes are least effective in peptizing hydrous oxides.

This theory explains a large mass of data which are not discussed in detail in this article, but which may be found in the references and elsewhere in the literature.

One final piece of evidence has contributed considerable weight to the complex compound theory. That is the evidence presented by those who have prepared metallic hydrosols by the Bredig arc method. This method of preparation has been looked upon by many chemists as a purely mechanical process, in which extremely fine particles of metal are dispersed in an aqueous medium by means of the electric arc. S. W. Pennycuik (13), who has prepared platinum hydrosols under a variety of conditions and by several methods, has come to the conclusion that the Werner theory and its modern extensions offer the only consistent explanation for the facts observed in platinum hydrosols. Likewise Pauli (12) has adopted the Werner theory and its modern extensions to explain the behavior of gold hydrosols prepared by the Bredig arc method. Thus the Bredig arc method need no longer be looked upon as a purely physical process of dispersing fine particles of metal in water, but as a process in which definite chemical compounds are formed which, like other complex compounds, have very definite ways of behavior.

#### SOME APPLICATIONS

If the complex compound theory had no practical applications it would still be very interesting, but it is gratifying that important applications have been found. Two of these will be mentioned because there is considerable experimental evidence for the conclusions given.

The field of leather chemistry has always been an important and interesting one. However, the art of leather tanning got far ahead of the science until about 1924, when Stiasny in Germany and Gustavson in this country adopted the Werner theory as a working basis for explaining the process of chrome tanning. Gustavson (7) explained the tanning of leath-

ery by the chromic sulfate method as due to the formation of a sulfato-hydroxo-chromi-collagen complex compound. This theory concerning the mechanism of chrome tanning threw immediate light on other operations, such as pickling, liming, and vegetable tanning of hides. It has been a matter of practical knowledge for years that Rochelle salts will detan leather. Since tartrate ion is more powerful than sulfate ion in displacing coordinately bound groups, the stripping of the tanning agent can be explained on the same basis as other displacements from complex compounds. Gustavson (7) actually assigns a structure to the complex formed in chrome tanning as being similar to the class of compounds known as chelate compounds. This is reasonable because diamines are well known for their tendency to form chelate complex compounds with metallic ions. Therefore the complex compound theory has been most helpful in understanding the mechanism of the processes of one of our largest industries and in predicting ways to improve the quality of leathers.

There is another field which has not been so well worked out as leather tanning but is very promising. That is the field of mordant dyeing. It is well known that many dyes require a mordant to dye cotton and wool cloth successfully. These mordants are usually hydrous oxides of aluminum, chromium, or iron. Sidgwick (17) has suggested that a chelate compound may be formed between certain dyes and hydrous oxides. Since there were about one hundred and sixty dyes listed in the 1914 edition of Schultz's Farbstofftabellen as being mordanted with ions of polyvalent metals, this field offers interesting possibilities. The complex compound theory should be very useful in this field, if the dye really forms a complex with the hydrous oxide. In the closely related field of lakes used in analytical chemistry there is also a possibility of interesting research in applying the complex compound theory.

In conclusion it may be said that the complex compound theory has been found very useful for explaining the behavior of metallic oxysalt hydrosols and their mode of formation. It is a relatively young theory and there is a wide field of experimental research open for testing the validity of this theory for explaining other colloidal phenomena.

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# ISOMERIZATION OF HYDROCARBONS

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Isomerization of hydrocarbons affords a study of intramolecular rearrangements in molecules which have only two different atoms. This type of reaction provides systems conducive to fundamental theoretical research, since the variable factors may be reduced to a minimum. Furthermore, it may play an important part in the petroleum industry, owing to the superior qualities of branched-chain to straight-chain isomers in gasoline, the many isomers present in the naphthene fractions, and the possibility of making available to industry many hydrocarbons which in the form of their less desirable isomers find little market. If the laws and conditions that govern isomerization become known, they should find wide application in the industrial field. An attempt has been made here to assemble the information relative to the isomerization of hydrocarbons.

## GENERAL DISCUSSION

### *Thermodynamic data*

It is only within the last few years that sufficient thermodynamic data have been accumulated to make the application of thermodynamic laws an important tool for hydrocarbon reactions. For the lower members of the paraffin and olefin series, very accurate values are now available, but other data involve uncertainties that allow only for an indication of the trends of reactions. These uncertainties arise largely from insufficient knowledge of the heat capacities and of accurate values for the heats of combustion. Isomerization reactions in the gaseous phase are important for many hydrocarbons, and heat capacity data in the gaseous state are known accurately in most cases only up to room temperatures. But even the accurate values often involved an extrapolation from 90° to 0°K., and this may make a contribution of from 10 to 15% of the total entropy. It is probable that this does introduce an appreciable error in some values. For hydrocarbons that are liquid at ordinary temperatures, the heat capacity data may be known experimentally for the liquid state, but for the gaseous state the data available are generally estimated values. Al-

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though, in general, thermodynamic data serve to indicate the trend in a particular reaction of hydrocarbons, the significance to be attributed to these uncertainties is an open question in the case of isomerization. For instance, are the differences in the free energies of the isomeric butanes, butenes, or heptanes real, and what are the limits of error?

Differences in the behavior of the isomeric hydrocarbons will depend on the distribution of energy in the rotational and vibrational states. The energy of a polyatomic molecule may be represented as the sum of the translational, rotational, vibrational, and electronic energies. Distribution of the energy in each form may be determined by the partition function, and since the entropy is proportional to the logarithm of the partition function, the entropy becomes an interesting property. Eidinghoff and Aston (23) have developed a method for calculating the classical partition function for the rotational energy. Kassel (64) has further refined the calculation of the determinant occurring in this partition function and has calculated the entropies of the isomeric butanes and butenes. The calculated entropies for the translational and rotational energies show that the vibrational energy contributes only a small part to the total entropy, but the exact amount has not been calculated. Moreover, the calculated translational and rotational entropies raise some question as to the accuracy of the experimental values, the correctness of the assumptions used for the statistical entropies, and a fundamental error in the third law.

#### *Equilibrium and velocity constants*

Relatively few equilibrium constants have been determined experimentally for isomerization reactions. Information about the equilibrium constant may be obtained from the thermodynamic properties. But since

$$\frac{\Delta H}{T} - \Delta S = R \ln K$$

the calculation for the equilibrium constant is concerned with the same thermodynamic properties as those considered above and encounters the same uncertainties. For a reaction with favorable thermodynamic properties and equilibrium constant, the desirability of a rate constant is obvious. From the kinetic viewpoint little is known about the isomerization of hydrocarbons. With only a few rate constant measurements available, there is need of a simple method of calculating the rate constant. Rice and Gershinowitz (100, 101) have used the statistical method for such a calculation where the collision factor in the reaction velocity constant contains the entropies for the different forms of energy. They have applied this method to the cyclopropane-propylene reaction and have found fair agreement if the shift of a hydrogen atom rather than the break-

ing of a carbon-carbon bond is the rate-determining step. Eyring (25) has used potential energy surfaces and the activating complex to calculate specific rate constants. This method holds much promise. For the *cis-trans* isomerization of  $\beta$ -cyanostyrene, however, the method appears to give a too small frequency for the torsional vibration around the double bond, according to Kistiakowsky and Smith (72). As yet both methods have not been tested sufficiently for us to know their real value for isomerization reactions. Kinetic measurements, particularly the *cis-trans* type, have been found difficult to interpret and to fit into the theories.

### *Catalytic action*

From experimental evidence the reasonable assumption may be made that isomerization reactions are slow reactions. This is logical, since in this type of reaction atoms shift their position in the molecule from one atom to another atom. If the action were energetic, the atom in this migrating process might travel to such a distance that instead of linking again to another atom it would leave the molecule and cause dissociation. It follows that for isomerization reactions to be of technical value, catalysts must be found to speed up the rate of transformation. Two types of catalysts have proven effective: namely, the solid and the liquid catalyst.

The solid catalyst is usually a metal, a metallic oxide, mixtures of metallic oxides, carbon, or silica. The reaction occurs on the surface of the solid and is related to the phenomenon of adsorption. Since solubility and surface in themselves can not explain adsorption, Taylor (121) has proposed the concept of activation energy as a theory of catalytic action. Experimental evidence of Taylor and coworkers supports this theory, for they found definite activation energies for the various reactions of hydrocarbons. For example, Turkewich and Taylor (128), working with magnesium oxide-chromium oxide and ethylene, found that there was a rapid reversible adsorption at 0°C. due to van der Waals forces; at 110°C. some activated adsorption occurred; at 184°C. decomposition accompanied the activated adsorption and ethylene was hydrogenated as well as decomposed; at 444°C. no hydrogenation occurred, as ethylene was decomposed rapidly. Methane, ethane, and propane showed the same type of adsorption, but the initial activation adsorption occurred at higher temperatures. It has been shown by Howard and Taylor (47), who have listed the activation energy for the van der Waals and hydrogen adsorption for the various metallic oxides and ethylene, that the activation energy varied for each catalyst. These authors have concluded for the hydrogenation of ethylene that the activity of the oxides will depend on the rate of activated adsorption.

Morikawa, Benedict, and Taylor (85) have studied the exchange reac-



tions of deuteromethanes and deuterioethanes and the reactions of methane and ethane with a nickel catalyst; Farkas, Farkas, and Rideal (26) have studied deuterioethylenes; and Polanyi and coworkers (45, 46) have worked with deuterobenzenes. All these studies indicate definite temperatures for activated adsorption which are characteristic for each type of reaction that the hydrocarbon undergoes. To account for these phenomena, Taylor has assumed activated dissociative adsorption of the hydrocarbon into fragments on the surface of the catalyst.

Good catalysts for isomerization reactions will cause only this type of reaction to occur, and for hydrocarbons this will involve either the carbon-carbon bond, the carbon-hydrogen bond, or both bonds. Presumably, the activation energy for isomerization reactions will be lower than for the other reactions of the hydrocarbons. Moreover, this activation energy will be characteristic of each hydrocarbon and each catalyst. If, then, the isomerization reactions are to occur to the exclusion of other reactions, such as replacement and decomposition reactions, there should be an appreciable difference between the activation energies of these reactions and the activation energies for other types of reaction. It would be expected that effective catalysts would fall into two classes: namely, those effective for the carbon-carbon bonds only, and those effective for the carbon-hydrogen bond only. Before the advent of the idea of activated energy, Lazier and Vaughan (76) applied the term "specific catalyst" to the catalyst which appeared to effect only one type of reaction. This use of specificity should not be confused with the above selective action of catalysts, for the above refers only to a specificity in a small range of the total activated adsorption. The application of the term "specificity" for this particular activated adsorption would lead only to confusion. Through the experimental data certain catalysts seem consistently to effect the shifting of a carbon atom or a hydrogen atom. These will be referred to as carbon-carbon or carbon-hydrogen isomerization catalysts. This is not a finely drawn distinction, for it should be remembered that in many cases the shifting of a carbon atom necessitates the shifting of a hydrogen atom as well. The above terms apply to catalysts where the rearrangement is determined by the initial shift of a carbon atom or a hydrogen atom. For rearrangements where the initial shift may be either atom, both types of catalysts should prove effective. The methylcyclopentane-cyclohexane conversion is an example of the latter.

For the liquid catalyst, where adsorption no longer holds, the forces between the catalyst and the hydrocarbon will have different characteristics from those of the solid catalyst, but the catalytic action may still be attributed to dissociation of the hydrocarbon into fragments under the influence of the catalyst. It might be pointed out that the average life

of these fragments has not been specified. For isomerization these shifts may take place almost instantaneously. With the solid catalyst in the liquid phase, such as aluminum chloride, which may or may not dissolve and has unshared electrons, the intermediate compound formation between the catalyst and hydrocarbon has been the popular theory. Olefins are known to form such addition compounds, but an attempt to carry the theory over to a general one for all hydrocarbons meets with difficulty. In the case of liquids, such as acids, many workers have for years accepted the formation of esters as intermediate compounds for the mechanism of the formation of olefins. An example of this is the reaction of phosphoric acid with ethylene. This reaction shows various activating steps, for at low temperatures ethylene may be driven off; at somewhat higher temperatures, higher olefins are formed; and at still higher temperatures, paraffins, naphthenes, and aromatics are formed. These steps correspond to the activation adsorption for particular reactions of a hydrocarbon with the solid catalyst. The theory of an intermediate compound necessitates the assumption of very short life for the ester during the ordinary reaction period. More recently, it has seemed to some workers that the assumption of catalytic dissociation into fragments is the simplest mechanism. This mechanism has advantages in that it is applicable to any type of hydrocarbon, that no assumption about the intermediate compound is necessary, that it is only a slight modification of the theory for thermal reactions, and that it is closely related to catalytic action of solids. This theory does not exclude the formation of esters or intermediate compounds, but it makes the formation of these a side reaction which will depend on the particular experimental conditions.

In the experimental data that follow, many references are to cases where isomerization is but one of several reactions occurring. These have been included not because the catalyst was considered a good catalyst, but because isomerization occurred under particular conditions. It is quite possible that under other conditions these poor catalysts might become good catalysts.

#### EXPERIMENTAL DATA

##### *Molecules with three carbon atoms*

The redistribution of energy in the simplest system of hydrocarbons is found in the cyclopropane-propylene isomerization. Accurate values for the thermodynamic quantities of propylene are available, but the values of cyclopropane involve estimated quantities. These data are given in table 1. The  $\Delta H_{298}^\circ$  value for propylene is taken from the value of Rossini and coworkers (103) for the heat of combustion of propane

and the value of Kistiakowsky and coworkers (68) for the heat of hydrogenation of propylene. The entropy value was obtained by Parks and Huffman (93) from the third law. The heat of combustion for the  $\Delta H_{298}^0$  value of cyclopropane is taken from Thomsen's value (123). This is somewhat higher than the value given by Kharasch (66) and is preferred, since Thomsen's values for propane and propylene are very close to the new values for these hydrocarbons. The entropy value is one estimated by Parks and Huffman (93). For the process cyclopropane  $\rightarrow$  propylene,  $\Delta H_{298}^0$  is equal to  $-6865$  cal. and  $\Delta F_{298}^0$  to  $-9275$  cal. This gives for the equilibrium constants at  $298^\circ$  and  $773^\circ\text{K}$ . the values  $5.83 \times 10^6$  and  $4.88 \times 10^8$ . These values can not be far from the true values in the order of magnitude even with the estimated quantities.

Assuming for temperatures around  $500^\circ\text{C}$ . that the only reaction taking place was cyclopropane  $\rightarrow$  propylene,—an assumption supported by the lack of a trend in the rate constants at constant pressure,—Chambers and Kistiakowsky (12) found that the thermal reaction was unimolecular and

TABLE 1  
*Thermodynamic data for isomeric hydrocarbons with three carbon atoms*

SUBSTANCE	$\Delta H_{298}^0$	$S_{298}^0$	$\Delta S_{298}^0$	$\Delta F_{298}^0$
	<i>15°-calories</i>	<i>E.U.</i>	<i>E.U.</i>	<i>15°-calories</i>
Propylene.....	4,475	63.1	-34.7	14,820
Cyclopropane...	11,340	55.0	-42.8	24,095

dependent on pressure. By extrapolation to infinite pressure, the high pressure constants or values of  $K_\infty$  at the temperatures  $469.6^\circ$ ,  $499.5^\circ$ , and  $518.6^\circ\text{C}$ . were 1.14, 6.08, and  $17.8 \times 10^{-4}$  sec. $^{-1}$ , respectively. The energy of activation was 65,000 cal., a value in good agreement with 63,900 cal., or that obtained by Trautz and Winkler (126). The value for the collision factor for the rate velocity constant differed by more than a power of 10 in the two experiments, and Chambers and Kistiakowsky attributed this to uncertainties in the temperatures used by Trautz and Winkler.

Rice and Gershinowitz (101) have found good agreement with the above rate constants for the calculated value obtained when using their statistical method, if the shifting of a hydrogen atom is assumed the rate-determining step. This does not tell the mechanism. These authors have pointed out that a carbon-carbon bond might break first. This might be followed by the establishing of an equilibrium between the activated molecules formed and the normal molecules. Finally, there might be a rearrangement into a propylene molecule or the rate-determining step. Since the

calculated value depends on the assumed mechanism of the reaction, the usefulness of this method of calculation is considerably restricted, and no definite conclusion may be drawn as to the mechanism of this simple isomerization reaction.

Thermal and catalytic studies, shown in table 2, have been made on the cyclopropane reaction with the one exception of the thermal experiment for the reverse reaction made by Engler and Rogowski (24). This is open to question. The thermal studies show that cyclopropane changes to propylene very slowly at as low as 20°C., but the rate increases with an increase in temperature. Catalysts increase the rate so that more than a 65 per cent conversion has been obtained. Platinum black, aluminum

TABLE 2

*Experimental data for isomeric hydrocarbons with three carbon atoms*

SUBSTANCE	TEMPER- ATURE	TIME	CATALYST	PRODUCTS	REFERENCE
	°C.				
Cyclopropane..	550	20 min.	ZnCl <sub>2</sub>	Propylene (30%)	(6)
Cyclopropane..	Room	5 months	Sunlight	No change	(118, 119)
Cyclopropane	100		KOH	Propylene (50-70%)	(53)
Cyclopropane..	200-315	90 min.	Pt black	Propylene (4.5-29%)	(57)
Cyclopropane..	350-360	105 min.	Al <sub>2</sub> O <sub>3</sub>	Propylene (15%)	(57)
Cyclopropane	370-385	105 min.	Al <sub>2</sub> O <sub>3</sub>	Propylene (20%)	(57)
Cyclopropane..	360-370	195 min.		Propylene (1-2%)	(57)
Cyclopropane..	100	120 hrs.	Pt black	Propylene (45%)	(118, 119)
Cyclopropane..	20	5 months	Pt black	Propylene (19-30%)	(118, 119)
Cyclopropane..	100	120 hrs.		Propylene (15-18%)	(118, 119)
Cyclopropane..	500	12-30 min.		Propylene (25-65%) (kinetic study)	(12)
Propylene.....	400		(a)	Cyclopropane (50%)	(24)

(a) Sealed tube.

oxide, caustic potash, and zinc chloride have been used as catalysts. If the shifting of the hydrogen atom is the rate-determining step, experimental work for platinum black and aluminum oxide is sufficient to suggest that these might be termed carbon-hydrogen isomerization catalysts, a suggestion that finds support throughout the following work.

#### *Molecules with four carbon atoms*

Thermodynamic data for the four-carbon atom hydrocarbons are the most accurate available for any group of isomeric hydrocarbons. These data are given in table 3. The data for butane have been obtained from the heat of combustion value of Rossini and coworkers (103) and from the entropy value of Parks and Huffman (93); those for isobutane have been

taken from Rossini's data (104) for the conversion of *n*-butane to isobutane, the data for butane, and Parks and Huffman's (93) predicted value for the entropy change. Parks and coworkers (96a) have made a recent recalculation of the entropy with a more careful extrapolation of the heat capacities and obtained slightly different values for the entropy of butane and isobutane. From the heats of hydrogenation obtained by Kistiakowsky and coworkers (68) and the entropy values of Todd and Parks (125), the data for the olefins have been obtained. The second series of values for isobutene were given by Parks and Huffman (93), and have been reproduced to emphasize how the more accurate values may completely reverse the information about the nature of a reaction.

TABLE 3  
*Thermodynamic data for hydrocarbons with four carbon atoms*

SUBSTANCE	$\Delta H_{298}^{\circ}$	$S_{298}^{\circ}$	$\Delta S_{298}^{\circ}$	$\Delta F_{298}^{\circ}$	$\Delta S_{298}^{\circ \dagger}$
	15°-calories	E.U.	E.U.	15°-calories	E.U.
Butane (g).....	-30,570	74.5†	-87.2	-4,580	75.37
Butane (g)*.....		75.8	-85.8	-5,000	
Isobutane (g).....	-32,200	69.4	-92.2	-4,720	71.25
Isobutane (g)*.....		70.0	-91.6	-4,900	
Butene-1 (g).....	-480	72.5	-57.9	16,780	72.47
<i>cis</i> -Butene-2 (g).....	-2,250	73.0	-57.4	14,860	68.22
<i>trans</i> -Butene-2 (g).....	-3,200	71.2	-59.2	14,450	67.61
Isobutene (g).....	-4,060	69.0	-61.4	14,240	68.21
Isobutene (g)§.....	-200	67.3	-62.8	18,500	

\* Recent recalculated values.

† See ref. 96a.

‡ Calculated translational and rotational entropy.

§ Old data.

In the last column appear the calculated values for the entropy due to translation and rotation as obtained by Kassel (64). Comparing the calculated and experimental values, Kassel concluded that since the estimated value for the vibrational contribution for normal butane is 2.79 E.U., giving a total entropy of 78.16 E.U., the experimental value obtained by Parks and Huffman appears to be too low. If the vibrational entropy for *n*-butane and isobutane is taken as approximately the same, the experimental value for isobutane is too low. Likewise, the experimental values of the entropy for butene-1 and isobutene are too low, and while the difference between the calculated values for *cis*-butene-2 and *trans*-butene-2 is of the right order of magnitude, the difference between the experimental values is too large. The differences between the experimental values and the calculated values may arise from the extrapolation

from 90° to 0°K., from an incorrect assumption of free rotation about the carbon-carbon bond in the statistical calculation, or from a finite entropy in the crystalline hydrocarbon at absolute zero. However, Parks and co-workers (96a) from their recent calculations rule out the possibility of error in the extrapolation from 90° to 0°K. for *n*-butane and isobutane, and believe that the difference in values is due to a fundamental error in the third law or to the statistical entropies.

From the data in table 3 the free energy, entropy change, and equilibrium constant have been calculated for the various isomerization reactions of these hydrocarbons and are given in table 4. At 298°K. the isomerization reactions listed in table 4 are spontaneous reactions. If the free energy is considered a linear function of the temperature, all the isomerization reactions 1 to 6, with the exception of reaction 3, which has a positive entropy change, will exhibit a limiting temperature for the spontaneous

TABLE 4

*Thermodynamic quantities for isomerization reactions of hydrocarbons with four carbon atoms*

REACTIONS	$\Delta F_{298}^0$	$\Delta S_{298}^0$	$K_{298}$
	<i>15°-calories</i>	<i>E.U.</i>	
<i>n</i> -Butane $\rightleftharpoons$ Isobutane	-140	-5.0	1.26 (1)
Butene-1 $\rightleftharpoons$ Isobutene	-2,540	-3.5	71.3 (2)
Butene-1 $\rightleftharpoons$ <i>cis</i> -Butene-2	-1,920	+0.5	25.2 (3)
Butene-1 $\rightleftharpoons$ <i>trans</i> -Butene-2	-2,330	-1.3	50.1 (4)
<i>cis</i> -Butene-2 $\rightleftharpoons$ <i>trans</i> -Butene-2	-410	-1.8	1.99 (5)
<i>cis</i> -Butene-2 $\rightleftharpoons$ Isobutene	-620	-4.0	2.83 (6)

reaction. Limiting temperatures for these reactions are 53°, 750°, 1819°, 255°, and 180°C., respectively.

For the isomerization of *n*-butane to isobutane the limit of error is of the same magnitude as the absolute value, and the older data indicate merely a spontaneous reaction at 298°K. The new recalculated data give the conversion of isobutane to *n*-butane as the spontaneous reaction. This reaction has not been studied directly. Ipatieff and Grosse (56) obtained isobutane in the presence of aluminum chloride and hydrogen chloride under pressure. Egloff and Parrish (19) have shown that the experimental data on stability favor isobutane as slightly more stable in the temperature range of 550-1100°C. If the entropy values at 298°K. are considered valid at the higher temperatures, the calculated order of stability is reversed at 53°C.; therefore it would appear that there is a slight error in the entropy values or that the specific heat may vary appreciably with higher temperatures. However, the new recalculated data

give *n*-butane as slightly more stable than isobutane at 298°K., with the stability of *n*-butane increasing rapidly with an increase in temperature. When the pressure was increased to 48.5 atm. at 555°C., the stability was doubled. The data at 48.5 atm. can not be used in strict comparison, since the thermodynamic data are for a constant pressure of 1 atm.

According to the thermal data of Hurd and Goldsby (50), the conversion of butene-1 to butene-2 occurred at 600–650°C. with a yield of 21 to 16 per cent, and that of butene-2 to butene-1 at 650–700°C. with a yield of 16 to 30 per cent. In both cases decomposition accompanied isomerization. Frey and Huppke (32) obtained an equilibrium mixture for butene-1, *cis*-butene-2, and *trans*-butene-2 of 25:40:30 at 350°C. From the thermal reaction of butane they obtained a 67:16:33 mixture at 375°C., and they believed that this was due to two end methyl groups in butane.

Catalysts have been found to speed up the conversion, as shown in table 5. In this connection it might be recalled that the butenes formed from butanol and the butyl halides (54, 80, 81, 99) vary in composition depending on the catalyst used. From the dehydrogenation of butanol, butene-1 was formed with the use of neutral or alkaline catalysts, and butene-2 with acid catalysts. Gillet (35) believed that in the case of the formation of butene-2, it was a result of the isomerization of butene-1 to butene-2. Matignon, Moureu, and Dole (80, 81) favor this view, and believe that they have shown experimentally that exceptions to this rule are due to traces of acid on the catalysts. Recently, Young and co-workers (134, 135) have pointed out that information favors the rearrangement of crotyl and methylvinylcarbinyl bromides when they are treated with the Grignard reagent or zinc in alcohol before the formation of the butenes. They rule out the possibility of isomerization of the butenes after their formation on the basis of the thermal experiments of Hurd and Goldsby and of Frey and Huppke. Since catalysts have a profound effect on the isomerization of the butenes, and since magnesium and zinc bromides, which are catalysts, were present during these reactions, the thermal data are not truly applicable in this case.

The isomerization of *n*-butene to isobutene is feasible up to 750°C., with an equilibrium constant of 71.2 at 298°C. Ipatieff and Pines (59) with phosphoric acid in the presence of hydrogen gas obtained small amounts of isobutane from butene-1. They believed that the isobutane obtained from butane in the work of Ipatieff and Grosse (56) resulted from the formation of butene-1 and its isomerization to isobutene, followed by hydrogenation to isobutane. The fact that isobutane was not obtained from *n*-butane with phosphoric acid as the catalyst, supported this contention. In the experimental data it is seen that when phosphoric

TABLE 5  
Experimental data for hydrocarbons with four carbon atoms

SUBSTANCES	TEMPERATURE °C.	TIME	CATALYSTS	PRODUCTS	REFERENCES
<i>n</i> -Butane.....				No change	(59)
<i>n</i> -Butane.....	175	3-4 hrs. (a)	H <sub>3</sub> PO <sub>4</sub>	Isobutane	(56)
Butene-1.....	500-650	40 sec.	AlCl <sub>3</sub> + HCl	Butene-2 (0-10.5%)	(50)
Butene-2.....	650-700	48-97 sec.		Butene-1 (11.7-7.5%)	(50)
Butene-1.....	249	206 sec.	H <sub>3</sub> PO <sub>4</sub> (b)	Butene-2 (100%)	(60)
Butene-1.....	21		HClO <sub>4</sub> (7%)	Butene-2 (21%)	(60)
Butene-1.....	76		C <sub>4</sub> H <sub>9</sub> SO <sub>2</sub> H (75% aq.)	Butene-2 (13%)	(60)
Butene-1.....	100		ZnCl <sub>2</sub> (75% aq.)	Butene-2 (5%)	(60)
Butene-1.....	427		H <sub>3</sub> PO <sub>4</sub> + Al <sub>2</sub> O <sub>3</sub>	Butene-2 (70-80%)	(60)
<i>trans</i> -Butene-2.....	100		H <sub>3</sub> PO <sub>4</sub> (100%)	Butene-1 (6.6%); <i>cis</i> -butene-2 (6%); <i>trans</i> -butene-2 (87.4%)	(60)
Butene-1.....	330	12 hrs.	H <sub>3</sub> PO <sub>4</sub> + H <sub>2</sub> O	Isobutane (6%)	(59)
Butene-1.....	400-600		CaO	Butene-2 (87%)	(107)
Butene-1.....	420		AlPO <sub>4</sub> + pumice	Butene-2 (92%)	(107)
<i>cis</i> -Butene-2.....	490-520	4.5-11.9 hrs.		<i>trans</i> -Butene-2 (kinetic study)	(71)
Methylcyclopropane.....	340-360	1.5-3 5 hrs.	Al <sub>2</sub> O <sub>3</sub>	Butene-2 (large); isobutene (small); propane (large); <i>tert</i> -butyl-1,1-dimethylethylene	(17)
Methylenecyclopropane.....	350		Al <sub>2</sub> O <sub>3</sub>	Butadiene	(83)

(a) 35 atm. (b) 7.18 atm. with impregnated diatomaceous earth. (c) 100 atm.



acid is a catalyst, a shift of a hydrogen atom occurs. If catalysts may be selective for the different types of bonds in isomerization reactions, phosphoric acid is probably a carbon-hydrogen isomerization catalyst. At 298°K. the order of increasing stability of the butenes is butene-1, *cis*-butene-2, *trans*-butene-2, and isobutene. If it is assumed that there is no appreciable change in the entropy at higher temperatures, this order is changed around 973°K. with the order of *cis*-butene-2 and isobutene reversed. For the butenes the experimental thermal data are not in complete agreement, as shown by Egloff and Parrish (19), but the data favor the order of stability given by the thermodynamic data at 298°K. However, in the work of Tropsch, Parrish, and Egloff (127), isobutene was found to be less stable than butene-1 at 1100°C. and 55 mm. pressure. According to the thermodynamic data at 1100°C., the free energies of butene-1 and isobutene are 79,016 and 80,242 cal., or, isobutene is less stable than butene-1.

The kinetics for the *cis-trans* thermal reaction has been investigated by Kistiakowsky and Smith (71), who found that the rate was dependent on pressure. With less than 1 atm. the conversion appeared to be a first-order homogeneous reaction. For pressures greater than 1 atm., the results were erratic and, in general, could not be satisfactorily explained. Their results confirmed the work of Hurd and Goldsby (50) at 650°C., in that the rate was slow with a rate constant of  $1.0$  to  $1.7 \times 10^{-6}$  sec.<sup>-1</sup> at 663–620°K. The equilibrium constant was 1.12, corresponding to 52.8 per cent of the *trans*-isomer (low-boiling). According to the thermodynamic data at 298°K., the equilibrium constant is 1.99, corresponding to 66.7 per cent of the *trans*-isomer. From the calculated entropy values for the translational and rotational entropy, Kassel obtained an equilibrium constant at 298.1°K. of 1.97, with a lower value predicted for the additional vibrational entropy. In the work of Hurd and Goldsby on the thermal reaction at 923° and 973°K., butene-2 was found to consist of 62 per cent of the *trans*-isomer (low-boiling) before pyrolysis and 61 per cent after pyrolysis. Also, butene-2 formed from butene-1 at the same temperatures showed 62 per cent of the *trans*-isomer. The entropy change for the conversion given by the work of Kistiakowsky and Smith was -1.2 E.U. at 663°K., as compared with -1.8 E.U. given by the work of Todd and Parks. From Kassel's calculated values the translational and rotational entropy would contribute -0.6 E.U. to the total entropy change for the reaction. An additional -0.6 E.U. for the vibrational entropy is plausible, but an additional -1.2 E.U., which would be necessary for a total change of -1.8 E.U., is out of line with the calculated or experimental data.

Effective catalysts for the isomerization of the butenes, where the re-

arrangement is due to a shift of a hydrogen atom, are catalysts of the acid or neutral type, as shown in table 5. Whether aluminum chloride actually caused the shift of a carbon atom in the paraffin is not known, but isobutane was obtained from butane when it was used. For the break in a three-membered ring, as in methylcyclopropane or methylenecyclopropane, aluminum oxide was effective. This same catalyst was used for the cyclopropane-propylene isomerization, where evidence favors the hydrogen shift as the rate-determining step.

*Molecules with five carbon atoms*

Although thermodynamic data are known for several hydrocarbons with five carbon atoms, uncertainties in some of the data and the lack of information on other isomers leave the thermodynamic picture incom-

TABLE 6  
*Thermodynamic data for hydrocarbons with five carbon atoms*

SUBSTANCE	$\Delta H_{298}^\circ$	$S_{298}^\circ$	$\Delta S_{298}^\circ$	$\Delta F_{298}^\circ$
	15°-calories	E.U.	E.U.	15°-calories
<i>n</i> -Pentane (g).....				-2,570
<i>n</i> -Pentane (l).....	-42,230	62.0	-132.2	-2,820
<i>n</i> -Pentane (l)*.....	-47,960	62.0	-131.9	-8,600
2-Methylbutane (l).....	-43,060	59.5	-134.7	-2,920
Neopentane (g).....	-38,460	72.9	-122.5	-2,300
Trimethylethylene (l).....	-17,050	59.5	-103.2	13,700
Methyl-1,4-butadiene (l).....	18,060	58.2	-73.5	39,970
Cyclopentane (l).....	-37,088	47.0	-116.0	3,235

\* Old data.

plete. These data are given in table 6. The source of the new data for *n*-pentane is the value of Rossini and coworkers (103) for the heat of combustion, and that of Parks, Huffman, and Thomas (96) for the entropy. The free energy of gaseous pentane was calculated by Parks (92). The heat of combustion values for the old data of *n*-pentane and 2-methylbutane are from Kharasch's value (66), and the entropy for 2-methylbutane from the data of Parks, Huffman, and Thomas (96). For neopentane the International Critical Tables (62) and Kharasch (66) give the same value for the heat of combustion. The molal entropy for the ideal gas at the boiling point, 286.6°K., has been determined by Aston and Messerly (3). This value of 71.7 E.U. is to be compared with 78.89 E.U. calculated from the Raman spectrum and moments of inertia. These authors believe that the discrepancy is real, and is due either to rotation of the methyl groups or to arrangements in the crystal. The value of

72.94 E.U. at 298°K. has been used to calculate the free energy. The data for trimethylethylene are from the estimated value of Parks and Huffman (93) for the heat of combustion and from their experimental value (94) for the entropy: those for methyl-1,4-butadiene are from the recent data for pentane, the value of Kistiakowsky and coworkers (69) for the heat of hydrogenation, and that of Parks, Todd, and Shomate (97) for the entropy. The data for cyclopentane are from the value for the heat of combustion given in the International Critical Tables (62) and from Parks and Huffman's estimated value (93) for the entropy.

Data for the isomeric pentanes are difficult to compare. Kharasch's value for the heat of combustion of *n*-pentane is definitely incorrect, and in view of this it is not safe to predict what changes more accurate data would give to those of other isomers. The magnitude of the correction made by the new data may be seen by comparing isobutene in table 3 and *n*-pentane in table 6. With the exception of the paraffins, the data for the hydrocarbons with more than four carbon atoms must not be taken too seriously. Where differences are involved in different types of hydrocarbons, the older figures may give a fairly accurate value, provided older figures are compared. As the interest here is often in small differences between the same type of isomeric hydrocarbons, the exact value of the data must be borne in mind.

The experimental data for these hydrocarbons are given in table 7. The isomerization of *n*-pentane to isopentane in the presence of catalysts, as carried out by Glasebrook, Phillips, and Lowell (36), suggests a greater thermodynamic stability for isopentane. This is in line with the data on the butanes. These investigators found that aluminum bromide, activated by small amounts of hydrogen bromide or hydrogen chloride, proved to be the best catalyst, being 11.4 times more active than aluminum chloride. Pentane gas streamed over aluminum chloride activated with hydrogen bromide gave a lower yield of isopentane but a higher yield of isobutane. Apparently aluminum chloride caused the *n*-pentane to split into smaller molecules to a greater extent than aluminum bromide. Egloff and Wilson (21) have pointed out that dry aluminum chloride or bromide has always been found an ineffective catalyst, but that traces of water, alkyl halide, or hydrated aluminum chloride were sufficient to start the reaction. The work of Glasebrook, Phillips, and Lowell agreed with these facts. Anhydrous aluminum oxide produced no action, but on the addition of hydrogen chloride the reaction started.

Hurd, Goodyear and Goldsby (51) found that the thermal reaction of pentene-1 yielded at 580-600°C. small amounts of pentene-2, trimethylethylene, *n*-butane, isobutane, and larger amounts of isopropylethylene. These workers found that pentene-2 underwent decomposition at 525-5

TABLE 7  
*Experimental data for hydrocarbons with five carbon atoms*

SUBSTANCES	TEMPERATURE °C.	TIME	CATALYST	PRODUCTS	REFERENCES
<i>n</i> -Pentane .....	Room		AlBr <sub>3</sub> ; HBr; HCl	Isopentane (56%); butanes (5%); high-boiling products	(36)
<i>n</i> -Pentane .....	40		AlCl <sub>3</sub> ; HBr	Isopentane (13.4%); butane (4-11%); isobutane (23-29%)	(36)
Pentene-1 .....	550-600	8-13 sec.		Pentene-2 (small); decomposition	(51)
Pentene-2 .....	550-600	12-19 sec.		Pentene-1 (small); decomposition	(51)
Pentene-2 .....	350-450		Al <sub>2</sub> O <sub>3</sub> ; H <sub>3</sub> PO <sub>4</sub> ; Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	No action	(91)
Pentene-2 .....	70-80	65 hrs.		Pentene-2 (transformed)	(110)
Isopropylethylene .....	450	16 sec.	Al <sub>2</sub> O <sub>3</sub>	Trimethylethylene (10%)	(91)
Isopropylethylene .....	500	14 sec.	H <sub>3</sub> PO <sub>4</sub>	Trimethylethylene (29%)	(91)
Isopropylethylene .....	425	16 sec.	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Trimethylethylene (47%)	(91)
Isopropylethylene .....	400-500	1 hr.		Trimethylethylene (traces)	(54)
Isopropylethylene .....	525-535	2 hrs.	Al <sub>2</sub> O <sub>3</sub>	Trimethylethylene (80%)	(54)
Isopropylethylene .....	400-500		Al <sub>2</sub> O <sub>3</sub>	Trimethylethylene (65%)	(54)
Isopropylethylene .....	500-505		Silica	Trimethylethylene (45%)	(54)
Trimethylethylene .....	520-530	70 min.	Al <sub>2</sub> O <sub>3</sub>	No action	(54)
Trimethylethylene .....	450	21 sec.	Al <sub>2</sub> O <sub>3</sub>	No isomers; polymers	(54)
Trimethylethylene .....	500	20 sec.	H <sub>3</sub> PO <sub>4</sub>		(91)
Cyclopentane .....	60	8 hrs.	AlCl <sub>3</sub>	No action	(15)
Dimethylcyclopropane .....	340-345	1.1 hrs.	Al <sub>2</sub> O <sub>3</sub>	Trimethylethylene	(57)
Ethylcyclopropane .....	300-310		Al <sub>2</sub> O <sub>3</sub>	Methylethylethylene	(106)
Methylcyclobutane .....	300-350	2 hrs.	Al <sub>2</sub> O <sub>3</sub>	<i>s</i> -Methylethyl-, isopropyl-, and <i>as</i> -methylethyl-ethylene	(106)
Methylenecyclobutane .....			HX	Methylcyclobutene	(31)
Methylenecyclobutane .....	300		Al <sub>2</sub> O <sub>3</sub>	Methylcyclobutene	(30)
Methylenecyclobutane .....	395-405	30 min.	Al <sub>2</sub> O <sub>3</sub>	Isopropylacetylene	(117)
Methylenecyclobutane .....	410-430	45 min.	Al <sub>2</sub> O <sub>3</sub>	Isoprene; polymers	(17)
Methylenecyclobutane .....			H <sub>2</sub> SO <sub>4</sub> ; HBr; alkali	Methylcyclobutene	(40)
Methylenecyclobutane .....	180-185		Sodium	Methylcyclobutene	(142)
Methylenecyclobutane .....	300		Al <sub>2</sub> O <sub>3</sub>	Methylcyclobutene	(61)

560°C., while Norris and Reuter (91) obtained no reaction at 350–425°C. in the presence of aluminum oxide, phosphoric acid, or aluminum sulfate. These catalysts were effective for the isomerization of isopropylethylene to trimethylethylene with yields as high as 65 per cent. The reverse process was not obtained with the same catalysts.

Sherrill, Ott, and Pickett (110) obtained a rearrangement of pentene-2 into another pentene-2 which they believed represented isomeric electromers, as postulated by Kharasch (67). The same transformation was effected by sunlight or ultra-violet light. When treated with hydrogen bromide the initial pentene gave 15 per cent of 3-bromopentane and 85 per cent of 2-bromopentane, while the transformed pentene gave 78 per cent of 3-bromopentane and 22 per cent of 2-bromopentane. They found no evidence of *cis-trans* isomerization and no shift of the double bond, and suggested that the halide derivatives may be a racemic or meso form of *cis-trans* isomers. Sherrill, Baldwin, and Haas (109) showed that pentene-2 made from 3-bromopentane was transformed by ultra-violet light but not that made from 2-bromopentane. Absorption spectrum evidence favored the existence of electromers and not *cis-trans* isomers, according to Carr (11). Sherrill (108a) believes now that this observed difference in the behavior of pentene-2 may be due to mixtures of *cis*- and *trans*-isomers of various compositions.

In the identification of the alkyl bromides, the refractive indices were used. Another method of identification has been developed by Lauer and Stodola (74), in which the halides were converted to the anilides and the percentage composition determined by the comparison of mixed melting points for known mixtures. By this method hydrogen bromide was found to add to pentene-2 to give equal amounts of 2-bromopentane and 3-bromopentane, where the method of preparation of pentene-2 made no difference in the products formed. Hence Lauer and Stoddard believe that there is no evidence to support the formation of electromers.

Derivatives of cyclopropane and cyclobutane have been shown to isomerize readily in the presence of a catalyst. With the three-membered carbon ring the ring was broken; with the four-membered carbon ring either the ring was broken, or a shift of the hydrogen between the side chain and the ring occurred when a double bond was present. Conditions which caused the breaking of the three-membered carbon ring often caused only a shift of the hydrogen atom in the four-membered ring.

The dehydration of isoamyl alcohol (91) gives the various pentenes with different experimental conditions and in line with the above data for the isomerization reactions. The same is true for tertiary-amyl alcohol (8, 111, 122), even though this necessitates a rearrangement of the carbon structure.

If the shift of the hydrogen atom is assumed to be the rate-determining step in the isomerization of the pentenes, the experimental data may readily be understood. Starting with pentene-1, the hydrogen atoms on the third carbon atom are the important ones, for if one hydrogen atom moves to the first carbon atom in the direction of the double bond, pentene-2 results. A shift of the same hydrogen atom in the other direction, to the fourth carbon atom, would give two methyl groups, which presumably may readily rearrange to give the isopropyl group or isopropylethylene. Since the chances for a hydrogen atom to move to the adjacent carbon atom are greater than its chances to move to the first carbon atom, isomerization to isopropylethylene should occur more readily than to pentene-2. In the experimental data there is little evidence for the formation of pentene-2. If the second hydrogen atom on the third carbon atom shifted, it would move only in one direction or toward the double bond, as in the conversion of isopropylethylene to trimethylethylene. This change occurs readily, as the experimental data show. Hence the experimental data support the following arrangement for the order of increasing thermodynamic stability: pentene-1, pentene-2, isopropylethylene, pentane, and isopentane.

The data suggest also that the stability of cyclo derivatives should be intermediate between that of the pentenes and the pentanes. No direct evidence is available for this, but the work of Cox (15) may be cited for indirect evidence. In the cracking of nonane in the presence of aluminum chloride for eight hours at 110–120°C., butane and cyclopentane were obtained. The author claimed experimental support for the formation of the latter from pentene. The above order of stability is in agreement with the order of thermal stability for the pentenes, according to Egloff and Parrish (19), but not for the pentanes. In the last instance, the thermal data are meagre.

In the isomerization of the pentenes, the effective catalysts were the type for carbon-hydrogen bonds, as shown in the case of the butenes. For the formation of isopropylethylene it is true that a carbon-carbon bond is broken, but in this case it appears to be a result of the initial shift of a hydrogen atom. For the isomerization of pentane to isopentane, since there is no point of unsaturation, the rate-determining step was probably the shifting of a carbon atom, and the effective catalysts were aluminum chloride or bromide. These catalysts appear to be carbon-carbon isomerization catalysts.

#### *Molecules with six carbon atoms*

The isomeric hexanes and hexenes have been used in very few investigations. Only thermodynamic data are available for *n*-hexane, hexene-1,

cyclohexane, and methylcyclopentane. These are given in table 8. The values in the International Critical Tables (62) for the heat of combustion of hexane, cyclohexane, and methylcyclopentane, the value of Huffman, Parks, and Barmore (48) for the entropy of hexane and methylcyclopentane, and the value of Parks, Huffman, and Thomas (96) for the entropy of cyclohexane have been used. The heat of combustion and entropy data for hexene-1 are values estimated by Parks and Huffman (93). Again, the order of increasing stability for the various types of hydrocarbons is olefin, cycloparaffin, and paraffin.

Nenitzescu and Dragen (90) and Ipatieff and Grosse (56) have recorded

TABLE 8  
*Thermodynamic data for hydrocarbons with six carbon atoms*

SUBSTANCE	$\Delta H_{298}^0$	$S_{298}^0$	$\Delta S_{298}^0$	$\Delta F_{298}^0$
	15°-calories	E. U.	E. U.	15°-calories
<i>n</i> -Hexane (l).....	-32,110	70.6	-155.6	-7,000
<i>n</i> -Hexene (l).....	-23,000	68.1	-127.1	14,900
<i>n</i> -Hexene (g).....				15,780
Cyclohexane (l).....	-36,700	49.2	-146.0	6,800
Cyclohexane (g).....				8,030
Methylcyclopentane (l).....	-37,800	59.2	-136.0	2,700

TABLE 9  
*Thermodynamic quantities for isomerization reactions of hydrocarbons with six carbon atoms*

REACTIONS	$\Delta F_{298}^0$	$\Delta S_{298}^0$	$K_{298}$	$K_{973}$
	15°-calories	E. U.		
Hexene-1 $\rightleftharpoons$ Cyclohexane	-8,100	-18.9	$5.25 \times 10^4$	$2.15 \times 10^2$
Hexene-1 $\rightleftharpoons$ Methylcyclopentane	-12,200	-8.9	$1.29 \times 10^7$	$3.23 \times 10^3$
Cyclohexane $\rightleftharpoons$ Methylcyclopentane	-4,100	-10.0	$2.45 \times 10^2$	$1.51 \times 10^1$

experiments in which isomeric hexanes have been obtained from *n*-hexane with aluminum chloride as the catalyst. Of the possible isomers only 2-methylpentane or 3-methylpentane were identified. Petrow, Meschitcherjakow, and Andrewjew (98) found that hexene-1 isomerized into hexene-2 and hexene-3 with molybdenum sulfide as a catalyst. From the experimental and thermodynamic data on the butenes and the pentenes, hexene-1 would be expected to form a number of isomeric hexenes.

Laughlin, Nash, and Whitmore (75) have shown that an equilibrium mixture of tetramethylethylene, *as*-methylisopropylethylene and tertiary-butylethylene in the ratio of 61:31:3 was obtained from any one of the

TABLE 10  
Experimental data for hydrocarbons with six carbon atoms

SUBSTANCES	TEMPERATURE °C.	TIME hours	CATALYSTS	PRODUCTS	REFERENCES
<i>n</i> -Hexane.....	100	7.5	AlCl <sub>3</sub>	2- or 3-Methylpentane	(90)
<i>n</i> -Hexane.....	69-72	3	AlCl <sub>3</sub> <sup>(a)</sup>	Gases; isobutane (90%); pentane (9%); isomeric hexanes; paraffins	(56)
Hexene-1.....	350-400	1	MoS <sub>3</sub> <sup>(b)</sup>	Hexene-2; hexene-3	(98)
Hexenes*.....	300	5-8	P <sub>2</sub> O <sub>5</sub> ; silica gel	Tetramethylethylene (61%); <i>as</i> -methylisopropylethylene (31%); <i>tert</i> -butylethylene (3%)	(75)
Cyclohexane.....	300-330	5-8	HI	Methylcyclopentane	(2)
Cyclohexane.....	250-260		HI; P	No change	(79)
Cyclohexane.....	740-750	1	Al <sub>2</sub> O <sub>3</sub>	Methylcyclopentane	(55)
Cyclohexane.....	500-510	4	Al <sub>2</sub> O <sub>3</sub> <sup>(c)</sup>	Methylcyclopentane; aromatics; naphthenes; olefins; methane	(55)
Cyclohexane.....	750	1		No change	(55)
Cyclohexane.....	135-145	6-8	AlCl <sub>3</sub>	No change	(37)
Cyclohexane.....	Low	48	AlCl <sub>3</sub> ; HCl	Methylcyclopentane	(2)
Cyclohexane.....	65-70	3	AlCl <sub>3</sub> ; 0.6% H <sub>2</sub> O	Methylcyclopentane (22.8%)	(89)
Methylcyclopentane.....	65-70	30	AlCl <sub>3</sub>	Methylcyclopentane (77.2%)	(89)
Cyclohexane.....	150	24	AlCl <sub>3</sub> ; HCl	Isobutane; methylcyclopentane; <i>m</i> -dimethylcyclopentane; dicyclohexyl; dimethylcyclopentyl	(58)
Cyclohexane.....	100	24	AlBr <sub>3</sub>	<i>cis</i> - and <i>trans</i> -Cyclohexane; methylcyclopentane; dimethylcyclobutane	(146, 149)

\* Each isomer gives same mixture.

(a) 35 atm. (b) 40 atm. (c) 110-112 atm.



isomers with phosphorus pentoxide on silica gel as the catalyst. The same equilibrium mixture was obtained with the same catalyst and tertiary-butylcarbinol (pinacolyl alcohol) by Whitmore and Meunier (132). Tetramethylethylene is symmetrical, while the other isomers are asymmetrical, and it would be expected that the latter would isomerize to tetramethylethylene. Moreover, tetramethylethylene will be the first product of isomerization from either *as*-methylisopropylethylene or tertiary-butylethylene. From the equilibrium ratio tertiary-butylethylene appears to have a highly unbalanced structure.

Thermodynamic data in table 8 predict that hexene-1 should form cyclohexane and methylcyclopentane. For these isomerizations and for the conversion of cyclohexane to methylcyclopentane, the thermodynamic quantities are given in table 9. For  $\Delta F_{298}^0$  the free energies for the liquid state have been used. These values for hexene-1 and cyclohexane are increased by 880 and 1230 cal., respectively, for the gaseous state. This might make a change in  $\Delta F_{298}^0$  for the reaction in the gaseous state, of not more than 400 cal. as a reasonable estimate. Although there are no direct measurements for the change of hexene-1 to cyclohexane, Egloff and Wilson (20) have shown that there is much evidence to support this isomerization in the reactions of the gaseous olefins. There are several studies of the change of cyclohexane to methylcyclopentane, and these are given in table 10. Even up to 750°C. the thermal conversion was not obtained, according to Ipatieff and Dowgelewitsch (55), but Nenitzescu and Cantuniari (89) claimed an equilibrium from both directions with 22.8 per cent methylcyclopentane at 70°C. in the presence of aluminum chloride. This does not agree with the equilibrium constants given by the thermodynamic data in the liquid state.

With the exception of hexene-1, in the experimental reactions of this group, both the carbon-carbon and the carbon-hydrogen bonds are involved. Aluminum oxide and aluminum chloride or bromide have been found good catalysts. The temperature range of reaction for aluminum oxide was 500–750°C., while for aluminum chloride or bromide the temperature range was 65–150°C. With aluminum chloride and the cyclohexane-cyclomethylpentane isomerization the isomer was the product at 65–100°C., but at 150°C. decomposition and alkylation accompanied isomerization. This would indicate that the shift of either a carbon atom or a hydrogen atom can be the rate-determining step in the mechanism.

#### *Molecules with seven carbon atoms*

The isomeric heptanes have been favored in that the thermodynamic data have been determined experimentally for all the isomers. These are given in table 11. The heat of combustion data for the group were

determined at the U. S. Bureau of Standards (66), and the molal entropies were made on the same samples by Parks, Huffman, and Thomas (96). The differences between the experimental values for the heats of combustion are not more than 1200 cal. This is the same as the magnitude of error for each value. At the time of the determinations Parks and Huffman assumed that there were no real differences in these values. The recent accurate data for the heat of combustion of *n*-heptane as determined by Rossini and coworkers (103) give a value for the free energy that is lower by an amount as great as or greater than the differences between the various isomers. With the recent data favoring a definite variation in the heats of combustion of the same type of isomeric hydrocarbons, it is quite

TABLE 11  
*Thermodynamic data for hydrocarbons with seven carbon atoms*

SUBSTANCE	$\Delta H_{298}^{\circ}$	$S_{298}^{\circ}$	$\Delta S_{298}^{\circ}$	$\Delta F_{298}^{\circ}$
	15°-calories	E. U.	E. U.	15°-calories
<i>n</i> -Heptane (1)*.....	-55,410	78.5	-180.9	-1,480
<i>n</i> -Heptane (1).....	-56,760	78.5	-180.4	-3,000
2-Methylhexane (1).....	-57,760	75.3	-183.8	-3,000
3-Methylhexane (1).....	-57,760	74.0	-185.1	-2,600
3-Ethylpentane (1).....	-56,760	74.6	-184.5	-1,800
2,2-Dimethylpentane (1).....	-58,760	68.1	-191.0	-1,800
2,3-Dimethylpentane (1).....	-57,760	72.4	-186.7	-2,100
2,4-Dimethylpentane (1).....	-57,760	69.7	-189.4	-1,300
3,3-Dimethylpentane (1).....	-58,760	70.1	-189.0	-2,400
2,2,3-Trimethylbutane (1).....	-58,760	64.8	-194.3	-800
Heptene-1 (1).....	-25,520	78.6	-149.5	19,050
Methylcyclohexane (1).....	-46,550	59.3	-168.4	3,600
1,2-Dimethylcyclopentane (1).....	-47,650	64.5	-163.2	1,000

\* New data.

possible that more accurate values for the heats of combustion might alter appreciably the information on some of the isomerization reactions, since the small differences in the free energies are highly significant for these reactions.

For the data on heptene-1 the value of Rossini and coworkers (103) for the heat of combustion of *n*-heptane with Kistiakowsky and coworkers' value (69) for the heat of hydrogenation and the value of Parks, Todd, and Shomate (97) have been used. The values of the heat of combustion for methylcyclohexane and dimethylcyclopentane are from the International Critical Tables (62), the entropy value for methylcyclohexane from Parks and Huffman (94), and the entropy value for dimethylcyclopentane from Huffman, Parks, and Barmore (40).

TABLE 12  
*Experimental data for hydrocarbons with seven carbon atoms*

SUBSTANCES	TEMPERATURE	TIME	CATALYSTS	PRODUCTS	REFERENCES
	<sup>°C.</sup>	<i>hours</i>			
<i>n</i> -Heptane.....	100	10	AlCl <sub>3</sub> ; 1% H <sub>2</sub> O	1,3-Dimethylcyclopentane; methylcyclohexane; methylcyclopentane; propane; isobutane; bicyclopentaffin	(90)
<i>n</i> -Heptane.....	220	3	AlCl <sub>3</sub>	Isomers (8%)	(98)
<i>n</i> -Heptane.....	300-400	6-7	ZnCl <sub>2</sub> <sup>(a)</sup>	Isomers (27-18%)	(98)
<i>n</i> -Heptane.....	400	7	CuO; MoS <sub>3</sub> <sup>(b)</sup>	Isomers (15%)	(98)
<i>n</i> -Heptane.....	420	3-14	MoS <sub>3</sub> <sup>(c)</sup>	Isomers (4-11%)	(98)
<i>n</i> -Heptane.....	100	10	AlCl <sub>3</sub> <sup>(d)</sup>	<i>n</i> -Hexane (1%); 2-methylhexane (4%)	(10)
<i>n</i> -Heptane.....	96		AlCl <sub>3</sub> <sup>(e)</sup>	Isomers (5-6%); pentanes (4.6%); 2-methylpentane (3.4%); 3-methylpentane (2.0%); <i>n</i> -hexane (0.4%); 2,4-dimethylpentane (1.5%); 2,2,3-trimethylbutane (0.5%); 3,3-dimethylpentane (0.4%); 2-methylhexane (1.2%); 3-methylhexane (1.6%); polymerization products (24.4%)	(9)
Methylenecyclohexene.....	140	3	Quinoline hydroiodide; chinolin	Methylcyclohexene-1,2	(29)
Methylenecyclohexene.....	170-150	6-7	Benzoic acid	Methylcyclohexene-1,2	(29)
Methylenecyclohexene.....	300		Quinoline hydroiodide <sup>(f)</sup>	Methylcyclohexene-1,2	(139)

(a) 50-60 atm. (b) 60 atm. (c) 70 atm. (d) Added as 50 per cent initial. (e) 10 g. added every 2 min. (f) Sealed tube.

The data in table 11 are for the liquid state, and it is very probable that the heat of vaporization will contribute further small variations for the gaseous state. However, assuming a linear temperature relationship and using the old data for *n*-heptane, the data for the isomeric heptanes are applicable to the work of Calingaert and Beatty (9) given in table 12. With aluminum chloride as the catalyst, the following heptanes, listed in the order of decreasing yields, were obtained from *n*-heptane: 3-methylhexane, 2,4-dimethylpentane, 2-methylhexane, 2,2,3-trimethylbutane, and 3,3-dimethylpentane. This order would not be predicted from the thermodynamic data. However, Parks, Huffman, and Thomas do not claim accuracy for the molal entropy of 3-methylhexane or of 2,3-dimethylpentane, since these did not crystallize at 70°K. It should be remembered also that the separation of the isomers is a difficult problem, and that the amount of isomerization of heptane was small in order to exclude secondary reactions. Therefore no conclusions are warranted. Other studies on the heptanes have been qualitative in nature and some are open to question. Besides aluminum chloride, zinc chloride, cupric oxide, and molybdenum sulfide have been used as catalysts, but except in the case of aluminum chloride the isomers formed were not identified.

Since the order of thermodynamic stability of this group is heptenes, cyclohexane and cyclopentane derivatives, and heptanes, the formation of the naphthenes in the thermal or catalytic reactions can be accounted for if heptenes are identified. Unfortunately, these reactions have not been investigated. However, Nenitzescu and Dragen (90) have recorded isobutene, cyclohexane, and the methyl derivatives of cyclohexane and cyclopentane as products from *n*-heptane with aluminum chloride as the catalyst. These products speak strongly for the decomposition to olefins and the isomerization of the olefins. Reactions of paraffins in the presence of aluminum chloride are characterized by the formation of higher paraffins and in some cases with small amounts of unsaturates. It has been assumed that this is due either to the olefin adding to the paraffin or to the reaction proceeding largely by way of free radicals (21). Whether the term "free radical" or the term "fragment" is used would depend on how the definition of free radical specifies the average life of a free radical. The non-appearance of olefins may also be due in part to the isomerization to naphthenes. If the conditions under which the reaction is carried out are vigorous, the olefin formation will increase.

A less profound change has been studied in the methylenecyclohexane-methylcyclohexene system, where a hydrogen atom shifts between the ring and the side chain with a change in the position of the double bond. The catalysts for these isomerization reactions in contrast to the isomerization reactions of heptane are large complex organic molecules.

*Molecules with eight and more carbon atoms*

The thermodynamic information on the isomeric octanes is much the same in character as that for the heptanes, though fewer isomers have been studied. When the older data from the International Critical Tables (62) for the heat of combustion are replaced by the new data of Rossini and coworkers (103), the change in the free energy value amounts to more than the difference between the values for the free energy of the various isomers, as shown in table 13. The heat of combustion data for the other isomeric octanes are from Kharasch's values (66). But here again, as Parks and Huffman (93) have pointed out, the limit of error is of about the same magnitude as the variations between the isomers; in other words, there is no real difference between the  $\Delta H_{298}^0$  values. The molal entropy for *n*-octane was determined by Huffman, Parks, and Barmore (48) and that for hexamethylethane and 2,2,4-trimethylpentane by Parks, Huffman, and Thomas (96) with a small correction for the latter (97). It is

TABLE 13  
*Thermodynamic data for isomeric hydrocarbons with eight carbon atoms*

SUBSTANCE	$H_{298}^0$	$S_{298}^0$	$S_{298}^0$	$F_{298}^0$
	15°-calories	E. U.	E. U.	15°-calories
<i>n</i> -Octane (l)*.....	-62,260	86 0	-206.0	-850
<i>n</i> -Octane (g)*.....				1,520
<i>n</i> -Octane (l).....	-64,210	86 0	-205.5	-3,000
2,2,4-Trimethylpentane (l).....	-65,310	75 0	-216.5	-770
Hexamethylethane (s).....	-67,410	61.4	-230.1	1,200

\*New data.

highly probable that more accurate data for the heats of combustion will show significant differences between the isomers. The same prediction can be made for the octenes, although thermodynamic quantities for diisobutylene alone are available. Commercial diisobutylene is really a mixture of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 in the ratio of 4:1. These have been separated into low-boiling and high-boiling fractions, and the thermodynamic data obtained by Parks, Todd, and Shomate (97), where the value of Rossini and coworkers (103) for the heat of combustion of the parent paraffin and the value of Kistiakowsky and coworkers (69) for the heat of hydrogenation have been used.

The experimental data are extremely limited, for the only studies made on *n*-octane are those by Petrow, Meschitcherjakow, and Andrewjew (98); these studies are qualitative in nature, with no attempt made to identify the isomers. The results are given in table 14. Zelinsky and Levina (140) have identified the shifting of the double bond in 2,6-dimethyl-

octene-7 to the 6-position. For this, palladium in the presence of carbon dioxide was used as the catalyst. Since the temperature for this reaction was 200°C. and the catalyst was palladium, the octenes are undoubtedly sufficiently stable to furnish some very interesting isomerization reactions. However, the work of Whitmore and Stahly (131) on the dehydration of methyl-di-tertiary-butylcarbinol and that of Nasarow (88) on ethylisopropyl-tertiary-butylcarbinol showed that the higher olefins split and rearrange into smaller olefins in line with the experimental equilibrium data for these olefins. This indicates, as would be expected, that the higher olefins are less stable than the lower olefins and in the presence of a catalyst decompose readily. Nasarow (88a) has recently made a detailed study of the effect of structure on the products formed from large olefin molecules in the presence of a catalyst, 1-bromonaphthalene-4-sulfonic acid. All these reactions are accompanied by decomposition of the molecule. Nasarow believes that the initial olefin molecule loses a hydrogen atom; the free radical formed isomerizes and a hydrogen atom is added; finally, decomposition of either one or both isomers occurs. The products are not isomers usually, but olefins with a varying number of carbon atoms. It has not been definitely proven that isomerization actually precedes decomposition. Since this work has been with pure isomerization reactions, the results are not reproduced here.

Grignard and Stratford (37) investigated the action of aluminum chloride on the alkyl derivatives of cyclohexane. These reactions are all characterized by the formation of polymethyl derivatives of cyclohexane. The number of methyl groups which become attached to the ring is dependent on the number of carbon atoms in the original alkyl side chain. For the *o*- and *p*-dimethylcyclohexane and ethylcyclohexane, the meta isomer was obtained. It is rather surprising that aluminum chloride should cause the severing of the carbon-carbon bond in the side chain and apparently not attack the carbon-carbon bonds in the ring, for the paraffin is more stable than the cyclo structure. Since propane, butane, and isobutane were also formed with the propyl, butyl, and isoamyl derivatives, the alkyl group may break from the ring first and these fragments will be very unstable. Perhaps the break in the carbon-carbon bond once removed from the ring is the preferred break, and the released fragment is added to another carbon in the ring. This process might be repeated until the side chain contained only one carbon atom. There can be little doubt that a monoalkyl derivative, where the alkyl group is other than the methyl group, is less stable than the polymethyl derivative and that the differences between the free energies of the isomers will be small. This reaction is distinctly the shifting of the carbon atoms in the side chain and is brought about by aluminum chloride. It is another illustra-

TABLE 14  
*Experimental data for hydrocarbons with eight or more carbon atoms*

SUBSTANCES	TEMPERATURE °C.	TIME hours	CATALYSTS	PRODUCTS	REFERENCES
<i>n</i> -Octane.....	405-410	3	AlCl <sub>3</sub> <sup>(a)</sup>	Isomers (23%)	(98)
<i>n</i> -Octane.....	360	3	MoS <sub>2</sub> <sup>(a)</sup>	No change	(98)
<i>n</i> -Octane.....	440	3	MoS <sub>2</sub> <sup>(a)</sup>	Isomers (23.6%)	(98)
<i>n</i> -Octane.....	410	3	ZnCl <sub>2</sub> <sup>(a)</sup>	Isomers (13.3%)	(98)
2,6-Dimethyloctene-7.....	200		Pd + CO <sub>2</sub>	2,6-Dimethyloctene-6	(140)
<i>o</i> - or <i>p</i> -Dimethylcyclohexane.....	115-120	7	AlCl <sub>3</sub>	<i>m</i> -Dimethylcyclohexane	(37)
Methyl- or dimethylcyclohexane.....	120-130		AlCl <sub>3</sub> ; ZnCl <sub>2</sub>	No change	(148)
Ethylcyclohexane.....	115-120	8	AlCl <sub>3</sub>	<i>m</i> -Dimethylcyclohexane	(37)
<i>cis</i> ( <i>o</i> - or <i>p</i> -)Dimethylcyclohexane.....	170-175		AlCl <sub>3</sub>	<i>trans</i> ( <i>o</i> - or <i>p</i> -)Dimethylcyclohexane	(78)
<i>trans</i> ( <i>o</i> - or <i>p</i> -)Dimethylcyclohexane.....	170-175		As + Os	Tetramethylcyclohexane; butane; polymers	(78)
<i>m</i> -Dimethylcyclohexane.....	120-130	4	Ni + H <sub>2</sub>	No <i>cis</i> -form	(37)
<i>n</i> -Propylcyclohexane.....	135-145	7, 5	AlCl <sub>3</sub>	Trimethylcyclohexane; propane	(37)
Isopropylcyclohexane.....	130-145	7	AlCl <sub>3</sub>	Trimethylcyclohexane; propane	(37)
<i>n</i> -, <i>sec</i> -, <i>tert</i> -Butylcyclohexane.....	150-160	8	AlCl <sub>3</sub>	Tetramethylcyclohexane; butane	(37)
Amylcyclohexane.....	130-155	7	AlCl <sub>3</sub>	Isocamyl-, methyl-, and tetramethylcyclohexane; butane	(37)
Isocamylcyclohexane.....	130-140	5	AlCl <sub>3</sub>	Methyl-, pentamethyl-, and tetramethylcyclohexane; <i>n</i> -butane and isobutane	(37)
<i>cis</i> -Hydrindan.....	100	12	AlCl <sub>3</sub>	<i>trans</i> -Hydrindan	(145)
<i>cis</i> -Decalin.....	Room	22	AlCl <sub>3</sub>	<i>trans</i> -Decalin (only)	(147)
<i>cis</i> -Decalin.....	100	12	AlCl <sub>3</sub>	<i>trans</i> -Decalin; other products	(147)
<i>cis</i> -Decalin.....	175-210		AlCl <sub>3</sub>	Dimethylbicyclo[0.3.3]octane	(150)

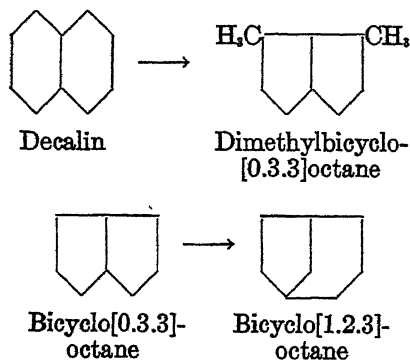
<i>trans</i> -Decalin.....	290-340	10-12	HI	Dimethylbicyclo[0.3.3]octane methylbicyclo[0.3.4]nonane Dimethylbicyclo[0.3.3]octane Bicyclo[1.2.3]octane <i>trans</i> -Decalin (best) No change Methylcycloheptane; octane (probably)	or 2-	(144)
<i>trans</i> -Decalin.....	130	24	AlBr <sub>3</sub>	Isostilbene		(117)
<i>cis</i> -Bicyclo[0.3.3]octane.....	Room	48	AlCl <sub>3</sub>	Stilbene		(117)
<i>cis</i> -Decalin.....	100	12	AlBr <sub>3</sub>	Stilbene		(117)
<i>trans</i> -Bicyclo[0.3.3]octane.....	200		Pt + H <sub>2</sub>	Isostilbene (6-8%) (kinetic study)		(70)
Cyclooctane.....	300	Short time	Pt	Stilbene (82-83%)		(70)
				4-Phenyl-2-butene; 1-phenyl-1-butene		(49)
Stilbene.....	Room	192	Ultraviolet light			
Isostilbene.....	170-180	1	CS <sub>2</sub> + Br <sub>2</sub> (trace)			
Isostilbene.....		Few minutes	HNO <sub>3</sub> vapor			
Stilbene.....	320-341					
Isostilbene.....	320-341					
4-Phenyl-1-butene.....	550	15 sec.				

(a) 70 atm.



tion in which aluminum chloride acts as a carbon-carbon isomerization catalyst.

Three bicyclic compounds are known to show isomerization reactions. These are the *cis* to *trans* isomerization of decalin and hydrindan, of decalin to dimethylbicyclo[0.3.3]octane and bicyclo[0.3.3]octane to bicyclo[1.2.3]octane. The latter two are given below. For the isomerization of decalin, the data of Zelinsky and Turowa-Podlak shown in table 14 are sufficiently complete to show the various steps in the activation energies. Thus, with aluminum chloride at room temperature, *trans*-decalin alone is formed; at 100°C. other products appeared with the *trans*-decalin; and at 175–210°C., dimethylbicyclo[0.3.3]octane was



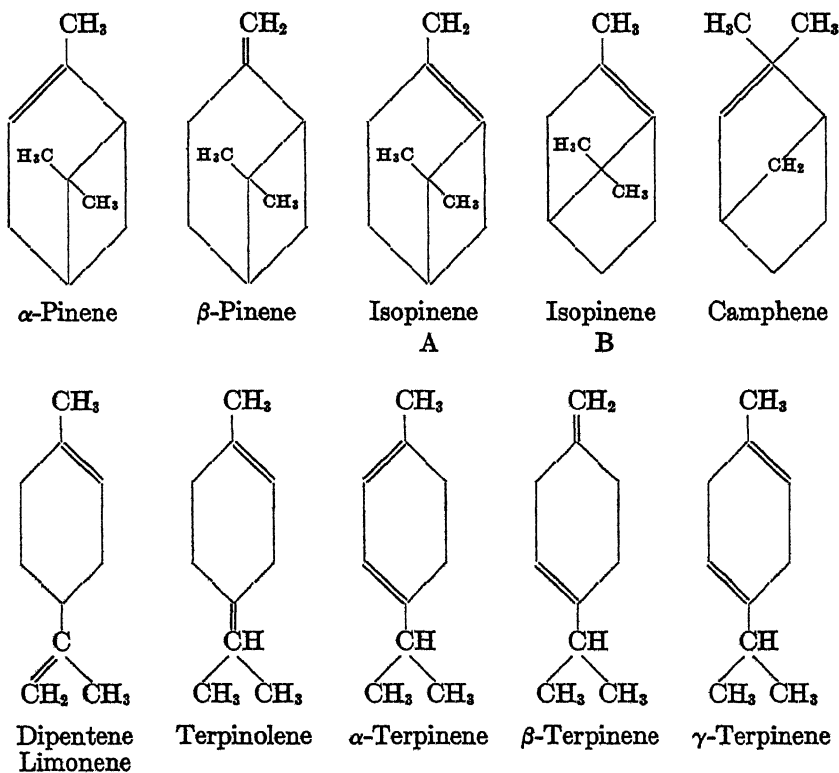
formed accompanied by decomposition. This same bicyclooctane was obtained at a somewhat higher temperature, 290–340°C., with hydrogen iodide as the catalyst. Aluminum bromide gave the best conversion of *cis*- to *trans*-decalin at 100°C. Jones and Linstead (63) obtained dimethylbicyclo[0.3.3]octane at 130°C. with aluminum bromide and a long contact time. While *cis*-decalin and *cis*-hydrindan isomerized into the *trans*-form, the *cis-trans* conversion of bicyclo[0.3.3]octane did not occur; instead there was a more deep-seated change to a five- and six-membered bicyclic compound, according to Barrett and Linstead (5). Thus with two six-membered rings, or with one six- and one five-membered ring, the *cis-trans* conversion occurred, but it did not occur with two five-membered rings. Zelinsky and Freeman (138) found also that cyclooctane isomerized and was dehydrogenated with platinum at 300°C.

Stilbene-isostilbene thermal isomerization gave an equilibrium of 83 to 94 per cent stilbene depending on the direction of approach, according to Kistiakowsky and Smith (70), who made a kinetic study of the reaction. This is of interest in that it involves rotation around the double bond and is closely related to the *cis*- and *trans*-butenes. Assuming the

entropy change for the reaction was equal to zero, the calculated  $\Delta H_{320}^0$  was 3000 cal. and the velocity constant  $6 \times 10^{12} e^{-42,800/RT}$ . The kinetic data showed inconsistencies for the *cis*- and *trans*-butenes, so that a comparison of this velocity constant of  $e^{-18,000/RT}$  with the above constant is not warranted.

### *Pinene and its isomers*

Pinene with a four-carbon atom ring and a six-carbon atom ring in its structure provides for the formation of a number of isomers where the four-carbon atom ring may be broken or a double bond shifted between the side chain and the six-carbon atom ring. These isomers are shown structurally below. There is some confusion in the literature as to the



structure of isopinene; hence two forms are given here. Besides the structural isomers, these isomers often contain an asymmetrical carbon atom, so that optical isomers are formed. Of the structural isomers

TABLE 15  
Experimental data for pinene and its isomers

SUBSTANCE	TEMPERATURE °C.	TIME	CATALYSTS	PRODUCTS	REFER- ENCES
Pinene.....	250-270	Several days	H <sub>2</sub> SO <sub>4</sub>	Dipentene; polymers	(130)
Pinene.....	400	1 day	Pd(H <sub>2</sub> )	Isomers	(130)
$\beta$ -Pinene.....	Room	6 hrs.	Pd(H <sub>2</sub> )	$\alpha$ -Pinene	(102)
$\alpha$ -Pinene.....	Room	1 hr.	Trichlorophenol	Isopinene	(137)
$\beta$ -Pinene.....	145-160	30 hrs.	Pd(H <sub>2</sub> )	$\alpha$ -Pinene; bornyl ethers	(4)
$\beta$ -Pinene.....	150-170	6 hrs.	Pd(H <sub>2</sub> )	$\alpha$ -Pinene	(4)
$\beta$ -Pinene.....	145		Benzoic acid	Pinene; terpinene; limonene; bornyl ethers	(4)
$\beta$ -Pinene.....	160	12-20 hrs.	Salicylic acid	Terpenes larger than with benzoic acid	(4)
$\beta$ -Pinene.....	175-180	20 hrs.	Abietic acid	$\alpha$ -Pinene (97.6%)	(4)
$d$ -Pinene.....	217-237	10-4 hrs.		$d$ -Pinene (believed); dipentene (actually)	(114)
$d$ -Pinene.....	200	18 hrs.	Active carbon + steam	Dipentene (19-34%)	(14)
Pinene.....	300	Short	Active carbon + steam	Camphene	(33)
Pinene.....	200		Fuller's earth	Dipentene	(38)
$\alpha$ -Pinene.....	-20-158	4 hrs.	Fuller's earth	Terpinene; dipentene	(129)
Pinene.....	-20-room		Activated charcoal	Camphene	(39)
$\alpha$ -Pinene.....	145-150	1.5 hrs.		Limonene, dipentene, terpinene (75%); camphene (25%)	(84)
Pinene.....	200-300	13 hrs.	Al <sub>2</sub> O <sub>3</sub>	Camphene (traces); terpinene; dipentene; limonene	(36)
$\alpha$ -Pinene.....	300	Short	Cu chromite	Terpenes (30%)	(1)
$\alpha$ -Pinene.....	375	Short	Cu chromite	Terpenes (31%); dipentene (42%); allyl- locimene in terpenes	(1)
$d$ -Pinene.....	380-425	2.75-3.5 hrs.	ThO + pumice	Dipentene (55-65%); camphene	(13)
$d$ -Pinene.....	65-70		H <sub>2</sub> SO <sub>4</sub> ; H <sub>3</sub> PO <sub>4</sub>	Terpinolene	(13)
$\alpha$ -Pinene.....	22-37		H <sub>2</sub> SO <sub>4</sub> ; CH <sub>3</sub> COOH	Terpenes	(1)
Pinene.....	50	24 hrs.	H <sub>3</sub> PO <sub>4</sub> ; H <sub>2</sub> SO <sub>4</sub>	Camphene; limonene; terpinene; <i>p</i> - cymene; 1,4-cineole	(18)
$\alpha$ -Pinene.....	250	20 hrs.	HgCl + I + Al	Terpinolene	(34)

$\alpha$ -pinene, isopinene, and  $\beta$ -pinene bear the simplest relation, for here a hydrogen atom shifts from a side chain to the six-carbon atom ring, while the four-carbon atom ring remains unchanged. Structure A is assumed for isopinene. As seen in table 15, these changes occur with palladium saturated with hydrogen (102, 137); at a higher temperature, 145–170°C., with trichlorophenol, benzoic acid, or salicylic acid (4); or at a slightly higher temperature, 175–180°C., with abietic acid when almost a complete change from  $\alpha$ - to  $\beta$ -pinene occurred (4).

Dipentene was the preferred isomer when experimental conditions which break the four-carbon atom ring were used. The "preferred" isomer may mean the isomer recorded more frequently, for the separation and the identification of the isomeric terpenes is a difficult problem. Du Pont (18) has obtained the most information on these isomers with the use of Raman spectra, and has identified the terpene isomers shown above (p. 157).

For the thermal reaction at 200–237°C., Conant and Carlson (14) obtained dipentene and polymers from *d*-pinene. Smith (114) studied the kinetics of this reaction and thought he had obtained *dl*-pinene, but, as shown by Conant and Carlson, he had in reality obtained dipentene. Kasel (65) has made a correction in the kinetic data of Smith. Arbutzov (1) believed that he obtained the chain isomer, allocimene, but Charlton and Day (13) could find no evidence to support this transformation. In general, high temperatures, 200–400°C., are used with metals, metallic oxides, or mixtures of metallic oxides, while low temperatures, 50–70°C., are sufficient for acid catalysts. It should be pointed out that the acid catalysts in the latter case are either dilute inorganic acids or inorganic acids plus acetic acid or alcohol, while in the former case for the simpler isomerization, large organic acid molecules are catalysts. Of the inorganic acids Charlton and Day (13) found that phosphoric acid was much less effective than sulfuric acid; Austerweil (4) found that the temperature of reaction varied with the strength of the organic acid and that for very long contact times, twelve to twenty hours, the organic acid catalysts also produced a small amount of terpene isomers. Venable (129) found that silica gel, iron gel, and activated charcoal did not bring about the change of pinene to dipentene and terpinene, while fuller's earth did. Gallas and Montanes (33a) claimed that pinene gave dipentene but not camphene at 150–200°C. with silex, activated carbon, kieselguhr, or magnesium oxide.

Pinene and its isomers are a group of isomers that will probably have small differences in their energy values; yet the isomerization reactions among the isomers are real, as is the selective influence which is possible with certain experimental conditions.

*The acetylenes and diolefins*

The alkyl and aryl acetylenes and diolefin molecules are highly unsaturated molecules, and therefore are characterized by the hydrogen atoms shifting readily within the molecule without appreciable decomposition taking place. The free energy of acetylene is approximately 50,640 cal., as compared with 15,280 cal. for ethylene. There are no thermodynamic data for the substituted acetylenes, but there are some for the substituted ethylenes. Thus, the values for the free energy of butene-1 and of heptene-1 are 16,780 and 19,050 cal. These data indicate that the free energy of the straight-chain olefins varies only slightly, but the variation is toward an increase in the free energy with an increase in the length of the chain. The shifting of the double bond from the  $\alpha$ - to the  $\beta$ -position lowers the free energy, as shown by butene-2. The branching of the chain also lowers the free energy, as shown by isobutene and 2,4,4-trimethylpentene. From this it may be inferred that the substituted acetylenes would give similar variations, although possibly of greater magnitude. Accordingly, a shift from the alkyl acetylene-1 to the alkyl acetylene-2 would be predicted. Perhaps the unexpected is the ease of the reversibility of this change. The diolefins with adjacent double bonds have not been investigated thermodynamically. Kistiakowsky and coworkers (69) have shown from the heats of hydrogenation that adjacent double bonds exert an unstabilizing effect upon one another. There have been numerous experimental studies on the isomerization of the acetylenes and diolefins. These are given in tables 16 and 17.

Rearrangements take place among the alkyl acetylene-1, the alkyl acetylene-2, and the diolefin where the diolefin is usually considered the form intermediate between the acetylenes. In his early work Favorsky (27) concluded that the preferred structure depended on the nature of the alkyl group adjacent to the unsaturated bond. Thus, for the primary group, the acetylene form resulted, in which case there was assumed an unstable intermediate diolefin form; for the secondary alkyl group, the diolefin resulted; and for the tertiary alkyl group, no reaction occurred. This was extended later (28) to include the diolefin as the only possible form for the tertiary alkyl group, the acetylene as the form from the primary alkyl group, and either the diolefin or the acetylene forms for the secondary alkyl group. Most workers have reported the isomeric substituted acetylenes as the product from the primary alkyl group. There has been some objection to this on the basis of incomplete identification of products. This may be true in some instances, but the experimental conditions probably are a larger factor in determining the form obtained. For the diolefin to form from the acetylene only one hydrogen atom need change its position; and it is reasonable to expect that this

TABLE 16  
*Experimental data for acetylenes*

SUBSTANCE	TEMPERATURE °C.	TIME hours	CAATALYSTS	PRODUCTS	REFERENCES
Butine-1.....	170	16	KOH	Butine-2 (100%)	(27, 28)
Pentine-1.....	170	20	KOH	Pentine-2	(27, 28)
Pentine-2.....	100	4-5	Na	Pentine-1	(27, 28)
Hexine-2.....	100-160		Na	Hexine-1	(27, 28)
Isopropylene.....	170	6	KOH	Dimethylallene	(27, 28)
<i>tert</i> -Butylacetylene.....	170-200		KOH	No action	(27, 28)
Butine-1.....	170	18-20	KOH	Butine-2 (<100%)	(133)
Octine-2.....	160	2	NaNH <sub>2</sub>	Octine-1 (80%)	(7)
Octine-3.....	170	9	NaNH <sub>2</sub>	Octine-1 (55%)	(7)
Nonine-2.....	160	2	NaNH <sub>2</sub>	Nonine-1 (80%)	(7)
Cyclohexylacetylene.....	140	10	KOH	Cyclohexeneethylenes	(22)
Cyclohexylbutine-2.....	160	3	NaNH <sub>2</sub>	Cyclohexylbutine-1 (80%)	(7)
Cyclohexylpentine-2.....	160	10	NaNH <sub>2</sub>	Cyclohexylpentine-1 (80%)	(7)
Cyclohexylhexine-2.....	160	10	NaNH <sub>2</sub>	Cyclohexylhexine-1 (80%)	(7)
Phenylpropine-2.....	110	2	NaNH <sub>2</sub>	Phenylpropine-1 (75%)	(7)
Heptene-1.....	360-420		Fe tube + soda lime	Heptene-2	(44)
Heptene-1.....	380		Fe tube + soda lime	Heptene-2 (70%)	(38)
Heptene-1.....	350		Fe tube + pumice	Heptene-2 (32%)	(38)

TABLE 17  
*Experimental data on diolefins*

SUBSTANCE	TEMPERATURE °C.	TIME	CATALYSTS	PRODUCTS	REFERENCES
Dimethylallene.....	100	3-4 hrs.	Na Floridin	Isopropylacetylene	(27, 28) (112)
Dimethylallene.....	215-280			Isoprene (20%); isopropylacetylene (small)	
Dimethylallene.....	334		Floridin	Isoprene (20%); isopropylacetylene (60%)	(112)
Methylallene.....	205-330		Floridin	Biviny! (20.6%); ethylacetylene (3.4-3.9%)	(113)
Allene.....	500	86 sec.		Methylacetylene (2%); allene polymers (large)	(82)
Methylallene.....	400-550	13-20 sec.	Quinoline hy- drotiodide	Acetylenes (1%)	(52)
Dimethylallene.....	130-135			Isoprene; isopropylacetylene (small)	(73)
Cyclohexeneethylene.....	100		Na	Cyclohexylethylene; cyclohexyl- acetylene	(22)
Cyclohexeneethylene.....	170	10 hrs.	Benzoic acid Floridin	1-Vinylcyclohexene-1	(22)
Diallyl.....	325			Diprenpyl; polymers	(77)
Diisobutylene.....	205	4 hrs.	Floridin H <sub>2</sub> SO <sub>4</sub>	Diisoprenpyl; polymers	(77)
Geraniolene.....	100			$\alpha$ - and $\beta$ -cyclogeraniolene	(124)

would occur in short contact time thermal reactions, as the work of Hurd and Meinert (52) has shown. On the other hand, for the substituted acetylene-1 to isomerize to the substituted acetylene-2 or the reverse, two hydrogen atoms must shift. This should require more vigorous experimental conditions, such as the presence of a catalyst. This is supported by a number of experiments. The diolefin would be anticipated as the preferred form when the hydrogen atoms are held more tightly by a ring structure, as in the cycloaliphatic compounds. An example of this isomerization is found in the work of Egorova (22) on the conversion of cyclohexylacetylene to cyclohexylidene ethylene.

The work of Marvel and coworkers on the acetylenic ethanes (16, 41, 43, 108, 116, 120) has shown that these rearrange readily into isomeric compounds without catalysts. Although the structure of these rearranged isomeric compounds has not been proven definitely, evidence supports the diolefin structure. Recently, Sparks and Marvel (115) have shown that this rearrangement to diolefins is not limited to hydrocarbons, but occurs readily with the acetylenic halides and carbinols. Zeberg (136) has shown that phenylallene rearranges at once, as methylphenylacetylene was obtained from 1,2-dichloro-3-phenylpropane.

As catalysts for these reactions, sodium, sodium or potassium hydroxide, sodium or potassium ethylate, and sodamide have been used most extensively for the liquid phase. This has led to the popular explanation of intermediate compound formation as a mechanism for the reaction. Hill (44) and Guest (38) extended the work to the vapor phase and found the isomerization occurred readily. Guest attributed Favorsky's failure to obtain a reaction in the vapor phase to the low temperature which he used. Hurd and Meinert (52) obtained rearrangements with the thermal reactions. Besides, such substances as floridin, pumice, benzoic acid, and quinoline hydrobromide are effective catalysts. The only explanation which is inclusive of all these facts is the activated dissociation into fragments under the influence of the catalyst. Again it might be added that the life of these fragments may be extremely short. The process may be likened to a gradual increase in the amplitude of vibration of the atom until its approach to the neighboring atom is so close that it becomes attached to the new atom and does not return to the original atom. From this it follows that intermediate compound formation is not a requisite in the mechanism, but only a side reaction. Sodium salts can be formed and these decomposed to give the isomer, as in the work of Stampfli and Marvel (116), but undoubtedly the actual formation and the extent of the formation of the intermediate compound depend largely on experimental conditions.

It is noteworthy that in all this work the sodium and sodium compounds



cause only the shift of the hydrogen atom and not the shift of the carbon atoms. In line with the preceding evidence, these catalysts appear to be carbon-hydrogen isomerization catalysts when there is a point of unsaturation in the molecule.

#### SUMMARY

The recent thermodynamic data for the isomeric hydrocarbons and the experimental data on the isomerization reactions lend support to small, distinct variations in the free energy of the various isomers for each type of hydrocarbon. The early values for the heat of combustion are not sufficiently accurate to show these small variations. Moreover, it is probable that a small error is introduced into some values for the entropy by extrapolation from 90° to 0°K. in the determination of the heat capacity.

For the various types of hydrocarbons with five or more carbon atoms, the order of increasing thermodynamic stability at 298°K. is olefins, cycloparaffins, and paraffins.

The catalytic data offer several examples of definite activating energies for the various isomerization reactions. These activating energies are dependent on the catalyst used. This suggests that the action for any catalyst may be explained by the concept of activating energies with dissociation of the hydrocarbon into fragments under the influence of the catalyst.

The majority of the isomerization reactions which have been investigated involve the shifting of the hydrogen atom. Few catalysts are known that effect the shifting of the carbon atoms. This is usually a more profound change in the structure. Certain catalysts appear to cause consistently the shifting of a hydrogen atom or a carbon atom. These have been termed carbon-hydrogen and carbon-carbon isomerization catalysts.

The data are too meagre to give the order of stability for any one type of hydrocarbon, but they do indicate that for the olefins at 298°K. the stability is increased for the shifting of the double bond toward the center of the molecule and for a simple branching of the chain. A highly branched chain may cause great instability.

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# SOME ORGANIC REACTIONS INVOLVING THE OCCURRENCE OF FREE RADICALS IN SOLUTION

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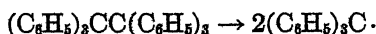
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## I. GENERAL INTRODUCTION

It has become quite evident today that there are two ways in which a covalent molecule may be disrupted during the course of a chemical change (151). *Either* the covalent bond is broken symmetrically

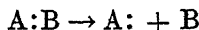


to yield two *neutral* atoms or radicals, each possessing an unpaired electron,<sup>1</sup> e.g.,

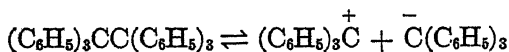
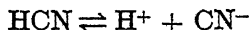


<sup>1</sup> Throughout this article a single dot, e.g.,  $A\cdot$ , represents one unshared electron; where specifically indicated a chemical bond, i.e., an electron duplet, is denoted by a dash.

or the covalent bond is broken unsymmetrically

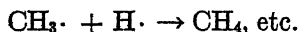
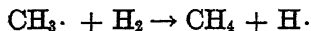
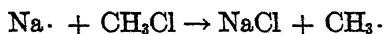


to yield two *ions* of opposite charge,  $A^-$  and  $B^+$ , e.g.,



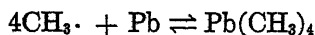
Subsequently, these initially formed activated radicals or ions interact with other similarly activated fragments, or with neutral molecules, to yield eventually stable molecular reaction products.

For reactions in the gaseous phase the former, or *atomic*, mode of dissociation is almost universal, and the neutral radicals produced by the initial decomposition of a reactant molecule either combine with each other upon collision, or, quite frequently, initiate a chain reaction which is consequent upon their collision with neutral molecules. This is typified by the reactions of atomic sodium in the vapor phase:



The investigations of Polanyi and others (24, 119, 111, 71, 135, 70, 80) of reactions initiated by free atoms in the gaseous phase have shown that in many cases a chemical change ensues *immediately* a free atom or radical collides with another molecule, and no extra "energy of activation" may be needed. Even with such stable organic vapors as those of methyl chloride or chlorobenzene the critical energy increment for reaction with a sodium atom is no more than 7000 to 9000 cal., which is very much less than the activation energy usually needed to bring about a chemical reaction between two molecules.

Since 1929, when Paneth and Hofeditz (114) first prepared the free radical *methyl*,  $CH_3\cdot$ , by heating lead tetramethyl in a rapid current of hydrogen at a pressure of 1 to 2 mm., and showed it to have a half-life period of  $6 \times 10^{-3}$  sec. by measuring the gradual decay of its reactivity with metallic lead or zinc,



it has been shown that the thermal decomposition of organic substances is a quite general process for the production of neutral radicals (125, 128). Thus Rice and his colleagues have shown that at a temperature of 800–1000°C. most organic substances can be broken down in the vapor phase

by a "cracking" process, in which simple aliphatic radicals such as methyl or ethyl are produced. Moreover, the requisite energy of activation is 75,000 to 85,000 cal., which is approximately the calculated value of the heat of formation of a carbon-to-carbon single covalent linkage.

Photochemical activation appears to be another general process for free radical formation. It has been studied most extensively with the vapors of aldehydes and ketones (see section III), which usually, but not invariably, eliminate the stable molecule, carbon monoxide, and yield free hydrocarbon radicals. Alkyl halides and the aliphatic azo compounds have also been shown to give free radicals by photochemical decomposition (7, 96), and research work in this field is developing with great rapidity at the present time.

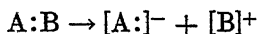
Whenever free radicals have been produced by the decomposition of the vapors of organic substances they have proved to be exceedingly reactive bodies. Not only do they combine instantly with metals such as lead, zinc, antimony, and mercury, and with non-metallic elements such as iodine and tellurium, but they will combine with each other on collision, even if cooled to the temperature of liquid air. Also, as previously mentioned, collision with a stable molecule will easily lead to chemical reaction, and the probability that an encounter with a molecule will occur with sufficient activation energy for chemical change is rarely less than one in ten thousand.

In view of this intense reactivity of the simple free organic radicals it is not surprising that their existence is hard to prove in any reactions occurring in the liquid phase, since a molecule in a liquid may undergo quite  $10^{14}$  collisions per second. Without exception the free neutral radicals, such as triphenylmethyl, which have been proved to exist for any appreciable time in solution, are complicated molecules in which the energy normally associated with the presence of a single unshared electron has been stabilized by resonance within the molecule. Thus Hückel (82) has calculated that in hexaphenylethane,  $(C_6H_5)_3CC(C_6H_5)_3$ , the binding energy between the two triphenylmethyl radicals is only about 13,000 cal. instead of the normal value of 79,500 cal. for the carbon-to-carbon link in ethane. Triphenylmethyl is in consequence a relatively stable compound, but its rapid reactions with sodium, iodine, and oxygen are nevertheless typical of a neutral radical possessing an unshared electron. For lack of experimental evidence one cannot dismiss as impossible the transient formation in solution of much simpler unstabilized free neutral radicals of high energy content, since quite a complicated sequence of chemical changes could occur in the short time interval of  $10^{-10}$  sec. or less, which is a maximum estimate for their mean free life. It is undoubtedly true, however, that free radicals are only produced in a small minority of reactions in solution,



for in most of the reactions of organic chemistry one can demonstrate that *ions* must intervene (151). The use of ionic reagents and of ionizing solvents is the rule and not the exception in organic chemistry, and indeed the whole theory of "polarity" for predicting and accounting for the courses and the relative rates of organic reactions can be built up on the hypothesis that the reactions of covalent molecules in solution normally involve the unsymmetrical ionic fission of a covalent link.

There is little doubt that a purely ionic fission of a covalent link,



involves more energy than a non-ionic fission,



since (a) an extra amount of coulombic energy must be required to separate the oppositely charged ions from an initial close proximity, and (b) gaseous molecules scarcely ever dissociate into charged ions (in the absence of electrons,  $\alpha$ -rays, or the like). In solution, however, every molecule is associated with the many others in its vicinity, and there is a mutual perturbation of the electronic fields. Both on account of the high dielectric constant of the solvent medium, and on account of the ease of formation of an electrical circuit of polar molecules, the energy required for the ionic fission of a covalent link in a dissolved substance may easily become much less than that required for the formation of neutral radicals. One has therefore to seek abnormal reactions of organic compounds in solution in order to discover any which might conceivably involve the transient formation of unstabilized free neutral radicals.

In the following sections a number of such reactions are discussed, and more of a similar type may be proved to exist in the future. From the foregoing introduction, however, it would appear probable (i) that neutral radicals are likely to be formed from those molecules which readily tend to undergo thermal self-decomposition at comparatively low temperatures, (e.g. explosives, endothermic compounds, etc.); (ii) that photochemical reactions are likely to involve free radical formation; (iii) that reactions in solvents containing ions or dipoles, or of high dielectric constant, are unlikely to proceed via neutral radicals, whilst reactions in non-polar solvents of low dielectric constant, such as benzene, carbon tetrachloride, or carbon disulfide, may do so; (iv) that a non-ionic fission of a covalent link will be improbable if the electrical dissymmetry (i.e., the dipole moment) of that link be large.

Molecules which readily undergo thermal self-decomposition at comparatively low temperatures have one structural characteristic in common. The heat of formation of certain of the covalent bonds must be small,

and one finds almost invariably that there can be eliminated either the stable atom of an element with a monatomic vapor, such as lead or mercury, or a simple molecule of high stability, such as nitrogen, carbon monoxide, or carbon dioxide.

## II. DECOMPOSITION OF ARYL ORGANOMETALLIC COMPOUNDS

With few exceptions the decomposition of organometallic compounds has been studied only in the vapor phase. Just as lead tetramethyl on heating yields lead and free methyl, so lead tetraphenyl yields the free phenyl radical. Dull and Simons (30) refluxed lead tetraphenyl with mercury and obtained some mercury diphenyl. Free phenyl may also be formed in the liquid phase from lead tetraphenyl, tin tetraphenyl, and mercury diphenyl, for on heating these substances in paraffin oil containing sulfur Razuviev and Koton (121) obtained diphenyl disulfide,  $C_6H_5SSC_6H_5$ , and inferred that free phenyl must have been produced. Hein and others (72, 74, 75) have also suggested that pentaphenylchromium hydroxide,  $(C_6H_5)_5CrOH$ , can eliminate a neutral phenyl radical in certain of its reactions.

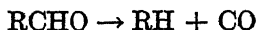
## III. DECOMPOSITION OF CARBONYL COMPOUNDS

Since 1932 the photochemical decomposition of aldehydes and ketones has been studied by Norrish and his collaborators at Cambridge (110, 108, 109, 106, 133, 6), who have concluded that the primary photochemical decomposition is the elimination of carbon monoxide with the production of neutral hydrocarbon radicals,

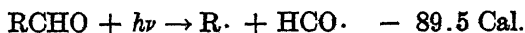


The presence of free neutral radicals in these photochemical processes has been established beyond doubt by the work of Pearson (115) and of Pearson and Purcell (116, 117), who have shown that the primary decomposition products were able to combine with metallic mirrors.

In the case of aldehydes, the final reaction is almost exactly represented by the equation,



and it appears that the free alkyl radical,  $R\cdot$ , and the free hydrogen atom,  $H\cdot$ , do not have any appreciable free existence. Norrish (105) has suggested that the two stages of the photochemical decomposition process



and

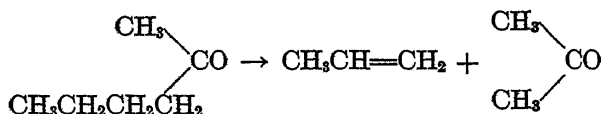


occur in such rapid succession that the  $R\cdot$  radicals and the  $H\cdot$  atoms never get free of one another's sphere of influence and are therefore eliminated as the single hydrocarbon  $RH$ .

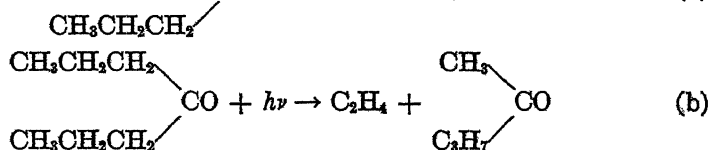
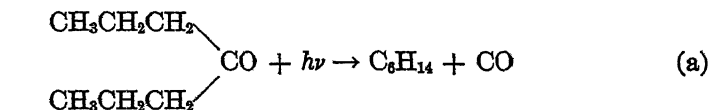
In the case of ketones, the free radicals mainly escape separately from the decomposing molecule, and in consequence can intermingle and form mixed products;



Higher aldehydes and ketones, however, tend to decompose differently (106, 6);



Quite recently the photochemical decomposition of ketones has been extended to the liquid state. Even in an inert solvent, such as hexane or cyclohexane, the photochemical decomposition of acetone will occur if the temperature is sufficiently high, but the free radical reacts with the solvent, as Bowen and Horton have shown (25). Norrish and Bamford (107) have shown that in the liquid state the decomposition of ketones with formation of carbon monoxide, which involves the production of free radicals (reaction a), is completely suppressed at low temperatures, but the decomposition by rupture of the hydrocarbon chain with liberation of an olefin (reaction b) can still occur.

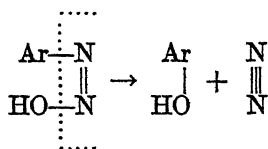


In a still more recent communication Norrish and Bamford (107a) have extended their study of the photodecomposition of ketones in solution, and disclose the interesting result that the free alkyl radicals disengaged in the photolysis do not combine together, as in the gaseous phase, but mainly react with molecules of the paraffin solvent by abstraction of hydrogen,  $R\cdot + R'H \rightarrow RH$ . The paraffin solvent then shows unsaturation. It is suggested that these results may indicate the occurrence of a continuous interchange of hydrogen atoms between paraffin molecules and free alkyl radicals, until two such radicals meet and react to give an olefin and a paraffin by disproportionation.

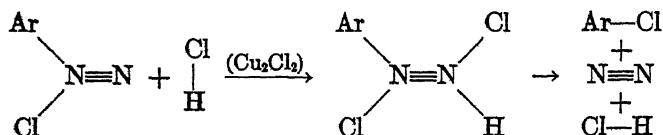
This property of alkyl radicals in solution is in striking agreement with the observations set out in this review of the characteristic properties of



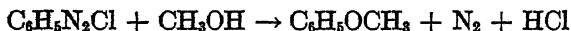
Of these diazo hydroxides (which are weak acids capable of forming easily hydrolyzed salts, the diazotates, with alkali metals) the compound with the *syn*-diazo structure was supposed to be unstable, owing to the ease with which it might eliminate a molecule of nitrogen, thus:



and in all decomposition reactions of diazo compounds it was suggested that the *syn*-diazo structure must have been formed, either by a tautomeric change, as depicted above, or by an addition reaction, represented as follows:



In addition to the fact that the geometrical structures assigned to the isomeric diazo hydroxides and their derivatives have not been confirmed experimentally, reaction velocity measurements have shown that this view is no longer tenable in all cases. For example Pray (120) has studied the decomposition of dry benzenediazonium chloride in a series of aliphatic alcohols and acids. It was found that for a series of aliphatic alcohols the reaction velocities, as measured by the rate of evolution of nitrogen, were all of the same order and in the case of the lower members of the series were practically identical (see table 1). Similar results were obtained with a series of aliphatic acids. Particular attention may be directed to the results obtained with methyl and ethyl alcohols, for although the reactions of benzenediazonium chloride with these two alcohols are to an appreciable extent qualitatively different, as shown by Hantzsch and Jochem (68),



yet the observed rate of reaction was identical in the two cases. The initial rate-determining process cannot therefore be, as Hantzsch imagined, the rate of decomposition of the addition compound with the *syn*-diazo structure, for this would depend on the nature of the alcohol ROH. These results, however, may be incorporated satisfactorily into a reaction mechanism involving the slow formation of free aryl radicals from the diazo compound,

or, more probably, from its wholly covalent tautomer. Under these circumstances the reaction velocity, measured by the rate of evolution of nitrogen, becomes the rate of formation of free aryl radicals, and this would be a unimolecular reaction, independent or practically independent of the second component, which is present in large excess and merely acts as a medium for the decomposition. The subsequent fate of the phenyl radical, whether it is converted into benzene, a phenyl alkyl ether, or some more complicated molecule, will have no bearing on the initial rate-determining stage.

Attention may also be directed here to the observation made by Möhlau and Berger (102) that 2- and 4-phenylpyridines are formed when dry benzenediazonium chloride decomposes in pyridine solution. This reaction

TABLE 1

*The rate of decomposition of benzenediazonium chloride in various alcohols and organic acids (Pray)*

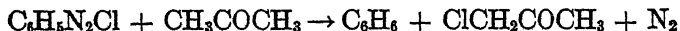
$$k' = 0.4343 k \times 10^4$$

SOLVENT	$k'$ AT 20°C.	$k'$ AT 30°C.	$k'$ AT 40°C.
Methyl alcohol.....	11.3	53.5	227
Ethyl alcohol.....	11.3	53.5	218
<i>n</i> -Propyl alcohol.....		52.0	204.2
<i>n</i> -Butyl alcohol.....		50.0	201
Isobutyl alcohol.....		54.0	208
Amyl alcohol.....		46.3	
Formic acid.....		18.6	73.1
Acetic acid.....		18.7	82.0
Propionic acid.....		18.9	82.0
Butyric acid.....		23.0	102.0
Water.....		25.0	107.0

seems to involve a non-ionic mechanism, probably through the agency of a free phenyl radical, since attack by phenyl cation and chloride anion would have resulted in the formation of phenylpyridinium chloride.

Quite recently Waters (153a) has found that when benzenediazonium chloride decomposes under acetone the metals antimony, bismuth, lead, and mercury are attacked even though the mixture is kept neutral with calcium carbonate. This experimental evidence affords strong support for the view, mentioned above, that free neutral radicals may also be produced in certain of the decomposition reactions of benzenediazonium chloride. Neutral radicals would not be produced from a diazonium salt, such as  $[C_6H_5N_2]^+Cl^-$ , unless the latter were converted into a covalent molecule, such as  $C_6H_5-N=N-Cl$ , before the fission of the nitrogen occurs. Otherwise the stable chloride anion would remain unchanged

throughout the whole of the decomposition process. The chloride anion does not attack the metals mentioned above and yet this decomposition reaction sets in at room temperature. Moreover, the principal reaction, in neutral conditions, between benzenediazonium chloride and acetone is



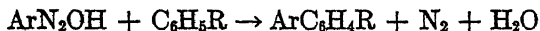
and the substitution of a hydrogen atom in the acetone molecule by one of chlorine again indicates that a reactive form of chlorine must be produced during the decomposition. The reaction between benzenediazonium chloride and acetone is quite evidently of the same type as the well-known reduction of a diazonium salt by an alcohol, for example:



After consideration of the newer experimental evidence set out in this review, there can be little doubt that the forty-year old theories of Hantzsch regarding the structural changes and decomposition reactions of the diazo compounds now need a thorough reëxamination, although as yet the newer hypotheses are only addenda to his general conceptions and do not conflict with them on any vital point.

#### V. REACTIONS OF DIAZO HYDROXIDES

The reactions between the diazo hydroxides (or diazo anhydrides) and neutral aromatic liquids have been studied by Gomberg and Bachmann (56) and by Gomberg and Pernert (58), who have developed thereby a useful method for the preparation of unsymmetrically substituted biaryls. According to these workers a moderately concentrated aqueous solution of the sodium diazotate is stirred vigorously in the cold with a neutral aromatic liquid. Nitrogen is evolved and a biaryl is formed in yields usually varying from about 5 to 40 per cent.



There is ample evidence to indicate that, as suggested by Gomberg and Pernert, the essential reaction of biaryl formation takes place in the non-aqueous medium. The diazo hydroxides being in general weak acids, their salts will suffer considerable hydrolysis in aqueous solution, and, according to these authors, "the success of the reaction is seen at once to lie in the ability of the non-aqueous liquid to extract from the aqueous layer the reactive diazo compound as fast as it is formed." The most characteristic feature of the reaction under discussion is the fact that in the formation of the biaryl the ordinary laws which govern aromatic substitution are not obeyed.

Aromatic substitution reactions are generally regarded as belonging to

one of two types. In the case of normal substitution by a cationoid reagent (e.g., nitric acid) groups such as the halogens, methyl, hydroxyl, and amino are said to be ortho-para directive, while groups such as nitro, carboxyl, aldehyde, and nitrile are said to be meta directive. On the other hand, for substituting agents which are anionoid in type (e.g. ammonia, potassium hydroxide) the normal orientation laws are reversed and the nitro group, for example, now becomes ortho-para directive (152). In the reactions studied by Gomberg, however, a third type of reaction is revealed, which will fit into neither of these categories and which appears to give rise to ortho-para substitution *irrespective of the nature of the so-called directing group*. For example, it was shown that from diazotized aniline and toluene, bromobenzene, benzonitrile, and nitrobenzene one obtained, respectively, 2- and 4-methylbiphenyl, 2- and 4-bromobiphenyl, 4-cyanobiphenyl, and 4-nitrobiphenyl. This remarkable feature, noted by Gomberg and Pernert, was encountered many years earlier by Kühling (93, 94), who from the sodium salt of diazotized *p*-nitroaniline and toluene obtained a compound proved by Kliegl and Huber (90) to be 4-nitro-2'-methylbiphenyl, while with nitrobenzene the product consisted of 4,4'-dinitrobiphenyl and 4,2'-dinitrobiphenyl. Further examples of this reaction have been recorded by Grieve and Hey (59, 60, 61), by Hey (77), and also by Cook and Cook (27).

The reactions which embrace aromatic substitution by either cationoid or anionoid reagents are clearly polar in type, whereas the formation of biaryls from the diazo hydroxides in all probability involves a non-polar mechanism. This conclusion is supported by a recognition of the conditions under which the reaction is effected and also by the unique characteristic of invariable ortho-para substitution, which would be difficult to explain on any polar basis.

A further reaction of benzenediazo hydroxide, which is of particular interest in connection with the reactions discussed in the later sections, is that in which carbon tetrachloride is used in place of the aromatic liquid as used by Gomberg. In this case an appreciable quantity of *chlorobenzene* is formed.<sup>2</sup> Another characteristic feature of these reactions is the frequent replacement of the diazo group by hydrogen. Reference to this property is made in later sections.

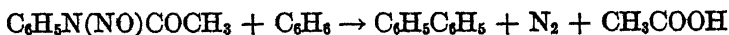
#### VI. REACTIONS OF NITROSOACYLARYLAMINES

Closely related to the diazo hydroxides are the *N*-nitrosoacylarylamines formed by the action of nitrous fumes on an acetic acid solution of an anilide. From acetanilide Fischer (37) obtained in this way nitroso-

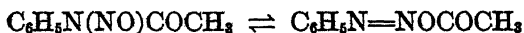
<sup>2</sup> Unpublished observation by D. H. Hey.



acetanilide, which was later used by Bamberger (5), who showed that in benzene solution nitrogen was evolved and biphenyl was formed:



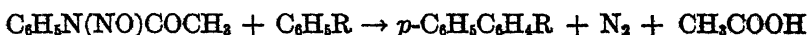
Bamberger (4), v. Pechmann and Frobenius (118), and Hantzsch and Wechsler (69) claim to have shown that nitrosoacetanilide is probably tautomeric with benzene *iso(anti)*-diaoacetate,



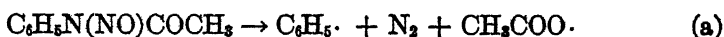
since it can also be obtained by acetylating sodium benzene diazotate with acetic anhydride. A close correspondence would therefore be expected between the reactions of the diazo hydroxides studied by Gomberg and the reactions of nitrosoacylarylamines.

Such a correspondence has in fact been revealed by Grieve and Hey (61), who have shown that when nitrosoacetanilide reacts in turn with toluene, chlorobenzene, nitrobenzene, and benzaldehyde, 4-methylbiphenyl, 4-chlorobiphenyl, 4-nitrobiphenyl, and biphenyl-4-aldehyde, respectively, are formed. The phenyl group enters the aromatic nucleus at the para-position in each case.

The reactions with nitrosoacetanilide lend themselves more readily to critical study than do those using diazo hydroxides, since they take place wholly in a homogeneous organic medium. If, as in the case of the diazo hydroxide reactions, the formation of the biaryl is dependent upon the production of a free phenyl radical as the first stage in the reaction mechanism, then the rate of evolution of nitrogen should be practically independent of R in the equation:



Measurements of the rate of evolution of nitrogen were made in benzene, toluene, *m*-xylene, mesitylene, chlorobenzene, anisole, and nitrobenzene, and it was shown that good unimolecular velocity constants were obtained, which varied but little from case to case (61). This is illustrated in figures 1 and 2, in which  $\log [V_\infty / (V_\infty - V_t)]$  is plotted against  $t$ , where  $V_\infty$  is the final observed volume of nitrogen,  $V_t$  the volume at time  $t$ , and  $k$  the unimolecular velocity constant. The reaction with the second component  $\text{C}_6\text{H}_5\text{R}$  (solvent) is thus secondary, involving one of the products, namely the free phenyl radical, of the primary unimolecular rate-determining stage. The reaction may therefore be more correctly written thus:



Significant also is the fact that the rate of evolution of nitrogen from nitrosoacetanilide in carbon tetrachloride solution is also of the same order,

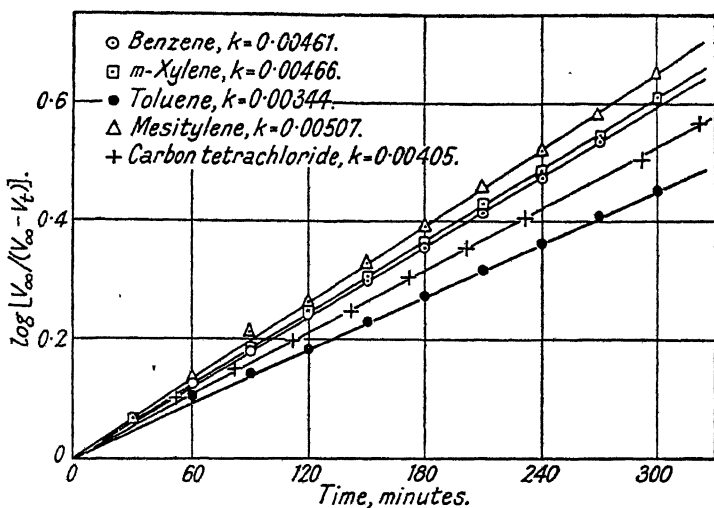


FIG. 1. Rate of decomposition of nitrosoacetanilide in various solvents. (From Grieve and Hey: J. Chem. Soc. 1934, 1800).

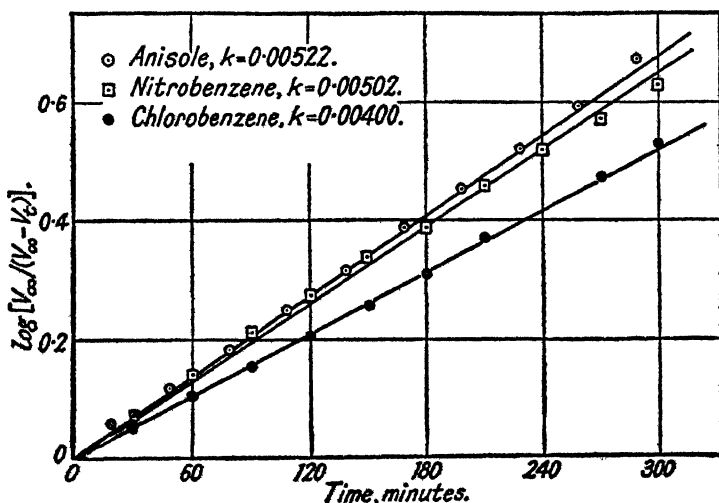


FIG. 2. Rate of decomposition of nitrosoacetanilide in various solvents. (From Grieve and Hey: J. Chem. Soc. 1934, 1800).

being practically identical with that in chlorobenzene solution. The qualitative nature of this reaction must of course be vastly different from those

in which biaryl formation results, but the final products are independent of the rate-determining reaction (reaction a), which seems to take place in all neutral media.

Further evidence for the non-ionic nature of the nitrosoacetanilide reactions has been provided by Waters (153), who allowed dry nitrosoacetanilide to decompose in a number of varied anhydrous solvents at room temperature. From reaction in *n*-hexane, cyclohexane, diethyl ether, dioxane, acetone, ethyl acetate, acetonitrile, and acetic anhydride, benzene was produced in each case, thus indicating the regular occurrence in non-aromatic hydrogen-containing solvents of the reaction:



This reaction recalls the formation of benzene by the decomposition of a benzenediazonium salt in ethyl alcoholic solution, which is customarily regarded as due to the action of a reducing agent. Further, with both methyl and ethyl iodides there was produced iodobenzene; with ethyl bromide and with bromoform there was produced bromobenzene; and with chloroform and carbon tetrachloride there was produced chlorobenzene. Thus in non-aromatic halogen-containing solvents the reaction may be represented:



The reaction with carbon tetrachloride recalls that previously recorded with benzenediazo hydroxide (p. 179).

Attention has also been directed by Waters to the other products which may be formed during the initial decomposition of nitrosoacetanilide into phenyl radicals and nitrogen gas. As represented above (reaction a) a neutral acetate radical is formed, which finally appears as acetic acid (reaction c). While it is true that acetic acid is formed in most cases, it has been known for some time that the amount formed is always somewhat less than that corresponding to the quantity of nitrogen evolved, as expressed in the simple equation. It was shown by Waters that in many cases carbon dioxide is also liberated. This confirms the transient existence of the neutral acetate radical,



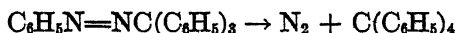
since an acetate anion never loses carbon dioxide at room temperature, except on discharge at an anode. Strong confirmatory evidence for the production of the acetate radical has been found in the fact that when nitrosoacetanilide decomposes in carbon disulfide or carbon tetrachloride solution metals, such as zinc, iron, copper, tin, lead, mercury, and antimony, may be attacked, giving rise to the formation of salts, princi-

pally the acetates. The metals are attacked even in the presence of an excess of calcium carbonate, so that the solution of the metal is not to be attributed to an attack by acetic acid molecules in presence of air. When the decomposition in presence of mercury was carried out in carbon tetrachloride solution mercuriphenyl chloride,  $C_6H_5HgCl$ , was also found as a reaction product; in benzene solution some mercurous acetate was formed.<sup>3</sup> These reactions with metals, many of which are normally inert, recall in striking manner the tests used by Paneth for free alkyl radicals. The reactions with mercury are particularly significant in this respect.

The reactions of nitrosoacetanilide thus enumerated are typical of free neutral radicals and cannot be satisfactorily explained through the agency of phenyl cations or anions.

#### VII. REACTIONS OF ARYLAZOTRIARYLMETHANES

The reactions of phenylazotriphenylmethane,  $C_6H_5N=NC(C_6H_5)_3$ , and of similar compounds have been studied by Gomberg and his coworkers (54, 57, 55) and more recently by Wieland and his coworkers (162, 157). Gomberg showed that when phenylazotriphenylmethane was heated above its melting point ( $111^\circ C.$ ) alone, admixed with sand, or in toluene or xylene solution, nitrogen was evolved and tetraphenylmethane was formed, but only in small yield:



Wieland and his coworkers studied the same reaction in greater detail and found that solutions of phenylazotriphenylmethane in specially purified light petroleum, xylene, or ethyl benzoate evolved nitrogen at about  $80^\circ C.$  with liberation of free triphenylmethyl radicals, which were identified spectrographically. The greater part of the free triphenylmethyl was isolated as the peroxide. In this reaction it is difficult and unreasonable not to admit, with the authors, the production of free phenyl radicals at the same time, thus:



The fate of the phenyl radical, however, remained obscure. Exhaustive search was made for biphenyl, which, it was supposed, would be formed from two phenyl radicals by polymerization, but none could be found. It was established that the phenyl radical was partly converted into benzene, which was isolated from the product when the reaction was carried out in highly purified light petroleum free from all aromatic hydrocarbons. The exact source which supplied the hydrogen remained unknown. The product also contained triphenylmethane and some

<sup>3</sup> Unpublished observation by J. W. Haworth and D. H. Hey.

tetraphenylmethane, the formation of the latter accounting for the destination of part of the free phenyl. The isolation of benzene in this reaction is very significant and is in agreement with the results obtained by Waters (153) in the reactions of nitrosoacetanilide with non-aromatic hydrogen-containing solvents described in the previous section. In similar manner the naphthylazotriphenylmethanes in *n*-hexane give rise to the production of naphthalene.

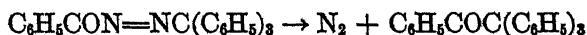
In order to make more complete the correspondence between the reactions of phenylazotriphenylmethane and nitrosoacetanilide, reactions of phenylazotriphenylmethane in aromatic solvents have been carried out by Hey (78). If the suggested free radical mechanism is common to the reactions of both types of compound, then in neutral aromatic solvents reaction should ensue between the phenyl radical and the solvent to give a biaryl compound. As predicted, when phenylazotriphenylmethane was allowed to decompose in benzene solution some biphenyl was formed, while in chlorobenzene solution some 4-chlorobiphenyl was formed. In an endeavor to extend the correspondence to include the reaction in nitrobenzene solution, only triphenylmethane could be identified in the product.

These results on the interaction of phenylazotriphenylmethane with aromatic solvents have since been confirmed and extended by Wieland and his collaborators (157). Thus, in reaction with toluene they obtained 2- and 4-methylbiphenyl, while with pyridine they obtained a mixture of phenylpyridines regarded as consisting of 2- and 4-phenylpyridine. The reaction with pyridine recalls that of Möhlau and Berger (102) using dry benzenediazonium chloride (see section IV). Further, Wieland showed that in carbon tetrachloride solution phenylazotriphenylmethane gave rise to chlorobenzene and triphenyltrichloroethane. The formation of chlorobenzene here is an exact reproduction of the result obtained by Waters with nitrosoacetanilide described above (section VI) and also of the reaction between benzenediazo hydroxide and carbon tetrachloride (section V). Similarly  $\alpha$ - and  $\beta$ -naphthylazotriphenylmethane in carbon tetrachloride give rise to some  $\alpha$ - and  $\beta$ -chloronaphthalene, respectively.

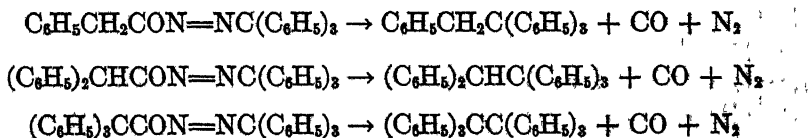
Among the more remarkable features of these reactions are the persistence with which the phenyl radical removes hydrogen from all non-aromatic hydrogen-containing solvents and itself becomes converted into benzene and, secondly and in contrast, the readiness with which biaryls are formed with aromatic solvents; the latter change involves the replacement and expulsion of a hydrogen atom. Wieland (157) has shown that when phenylazotriphenylmethane, admixed with sand only, is heated at 105–115°C. in a high vacuum some benzene is formed, together with tetraphenylmethane and triphenylmethane. One can only suppose here that part of the compound undergoes disruptive decomposition in order

to supply the hydrogen required. Again, in the thermal decomposition of *m*-phenylenebisazotriphenylmethane the bivalent phenylene radical also yields benzene. It is not certain, however, whether in this case the bivalent radical is formed as such, or whether the two molecules of nitrogen are eliminated successively. With regard to the replacement and expulsion of aromatically bound hydrogen, part of it becomes associated with triphenylmethyl as triphenylmethane, but it has also been shown that if phenylazotriphenylmethane is allowed to decompose in benzene solution containing some benzoquinone, in an atmosphere of nitrogen, there is formed, in addition to some phenylbenzoquinone and the di(triphenylmethyl) ether of hydroquinone, some quinhydrone, thus indicating the production of active hydrogen during the reaction. Further examples to illustrate these points are included in Wieland's communication, and from these it may be noted that, in general, as the complexity of the arylazotriphenylmethane increases there is a tendency in the reactions with benzene or toluene for the latter to serve merely as sources of hydrogen, in much the same way as the aliphatic hydrocarbons, and biaryl formation is less prevalent. This may be attributed partly to the greater difficulty attendant on the isolation of compounds of higher molecular weight which might be formed.

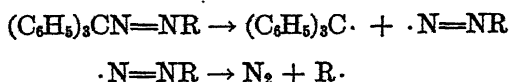
Wieland and his coworkers have also studied the reactions of acylazotriphenylmethanes (159, 158). They showed, for example, that when benzoylazotriphenylmethane was heated in xylene solution nitrogen was evolved and some benzoyltriphenylmethane was formed, probably through the agency of free radicals:



When the same decomposition was carried out in carbon tetrachloride solution the free benzoyl radical removed chlorine from the solvent, with formation of benzoyl chloride. Similar reactions were carried out with acetylazotriphenylmethane and other acylazotriphenylmethanes and, when effected in an atmosphere of oxygen, peroxides were formed from the triphenylmethyl radicals and in some cases from the acyl radicals also. It is interesting to note that as the hydrogen in the acetyl radical is successively replaced by phenyl there is an increasing tendency for the loss of carbon monoxide to occur (compare section III), according to the following equations:



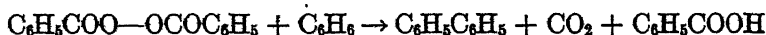
The greater yield in which benzoyltriphenylmethane is formed from benzoylazotriphenylmethane compared with the small yield of tetraphenylmethane obtained from phenylazotriphenylmethane, and other cognate facts, led Wieland to consider the possibility of a step-wise decomposition thus:



where R may be aryl or acyl. This may be equally possible in decomposition reactions of the diazonium salts and of the diazotates, since small yields of azo compounds are found as by-products in many of the reactions of these compounds (58, 31, 97, 23).

#### VIII. REACTIONS OF DIACYL PEROXIDES

When a solution of dibenzoyl peroxide in benzene is heated, carbon dioxide is evolved and biphenyl is formed, thus:



The participation of the solvent in this reaction is proved by the fact that di-*p*-chlorobenzoyl peroxide with benzene gives 4-chlorobiphenyl and not 4,4'-dichlorobiphenyl, and that in similar manner di-*m*-nitrobenzoyl peroxide with benzene gives 3-nitrobiphenyl and not 3,3'-dinitrobiphenyl (40). With dibenzoyl peroxide and toluene a mixture of the 2- and 4-methylbiphenyls is obtained (41). The reactions of the diacyl peroxides, however, are more complicated than the above simple equation would imply, and have been studied in great detail.

The fact that dibenzoyl peroxide is itself thermally unstable and can undergo reaction in an aromatic solvent to yield a derivative of biphenyl suggests that the reactions of the diacyl peroxides may have much in common with those of the diazo hydroxides, nitrosoacylarylamines, and arylazotriarylmethanes, and may decompose, with the elimination of the stable molecule carbon dioxide and production of free radicals, just as the diazo and azo compounds decompose with the elimination of the stable molecule nitrogen. In order to find out how far the resemblance extends, reactions were carried out by Hey (78) in which dibenzoyl peroxide was allowed to decompose in solution in chlorobenzene, nitrobenzene, and ethyl benzoate in turn. In chlorobenzene solution 4-chlorobiphenyl was formed, and with nitrobenzene both 2- and 4-nitrobiphenyl were isolated from the reaction product. The experiment with nitrobenzene is confirmed by Wieland, Schapiro, and Metzger (165). The phenomenon of *invariable ortho-para substitution* is therefore also a characteristic of the reactions of the diacyl peroxides. This receives further confirmation

from the observation, due to Overhoff and Tilman (113), that 2- and 4-phenylpyridine are formed during the decomposition of dibenzoyl peroxide in pyridine solution. It will be recalled that a similar reaction with pyridine has been observed with dry benzenediazonium chloride (see p. 177) and with phenylazotriphenylmethane (see p. 184).

When dibenzoyl peroxide undergoes decomposition in solution in ethyl benzoate, ethyl biphenyl-4-carboxylate is formed, together with some ethyl biphenyl-3-carboxylate (78). The isolation of the latter led to a more detailed examination of the product of the reaction between sodium benzenediazotate and ethyl benzoate, which revealed that, while the main product was ethyl biphenyl-4-carboxylate, smaller quantities of both the corresponding 2- and 3-carboxylic esters were also formed at the same time. The differences in reactivity usually shown between the ortho- and meta-positions in ethyl benzoate have not the clear demarcation found, for example, between the corresponding positions in nitrobenzene. The isolation of all three isomerides in the reaction with ethyl benzoate may be correlated with this fact, but it is not clear why, in general, reaction at the ortho- and para-positions should take precedence over reaction at the meta-positions in the reactions under discussion, and it might well be that a more exhaustive examination of the products in these reactions would reveal in every case the presence of all three isomerides. It is quite definitely established that in aromatic substitution both by cationoid and anionoid reagents the ortho- and para-positions are the most reactive, but when substitution is brought about through the agency of a free radical, as is here supposed, the position is not so clear. It has been pointed out, however, that the phenyl, or substituted phenyl group, which enters the aromatic nucleus has unique properties in that it is able to compensate electrostatic disturbances of either sign (83, 84). This amphoteric characteristic enables the group to function *as if it were* a potential cationoid or anionoid reagent, as occasion demands, and may be an important factor in influencing the course of the reaction. Further, mesomeric changes within any aromatic ring are confined to resonance structures in which the ortho- and para-positions, but not the meta-positions, have variable energy levels. The isolation of all three isomerides in these reactions, however, even if it proves to be general, in no way invalidates the argument put forward, the essential feature of which is a characteristic departure from the laws governing normal aromatic substitution.

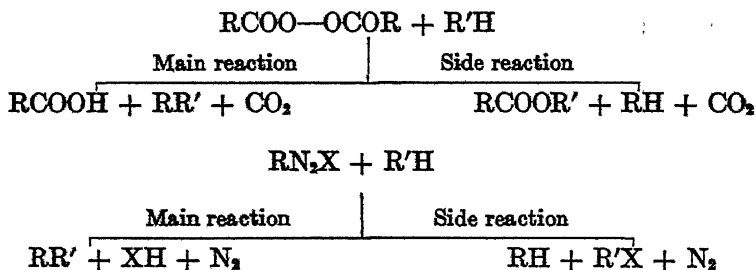
Gelissen and Hermans (40) have shown that the action of dibenzoyl peroxide on boiling benzene gives, in addition to biphenyl, carbon dioxide, and benzoic acid, smaller quantities of phenyl benzoate, terphenyl, and quaterphenyl. The formation of the latter hydrocarbons is a general feature of the reactions under discussion and has already been encountered



by Gomberg and his coworkers (56, 58) in their reactions with the diazo hydroxides. The presence of these polyphenyls must be attributed to the successive action of the peroxide or diazo hydroxide on the hydrocarbons initially formed. The same phenomenon was observed by Gerngross and Dunkel (47) and by Gerngross, Schachnow, and Jonas (48) in a study of the formation of biphenyl from diazotized aniline in the presence of copper by the method of Gattermann (39).

The reactions of dibenzoyl peroxide show further characteristics which simulate very closely those exhibited by the diazo hydroxides, the nitrosoacylarylamines, and the arylazotriarylmethanes. For example, Gelissen and Hermans (42, 43, 45, 46) have shown that in ethyl alcohol, isobutyl alcohol, acetic acid, 2-pentene, and cyclohexane, dibenzoyl peroxide decomposes to give benzene. Similar results were obtained by Böeseken and Gaster (20) from the action of dibenzoyl peroxide on light petroleum and on *n*-octane. These reactions constitute further examples of the removal of hydrogen from an aliphatic solvent by the phenyl radical. Again, Böeseken and Gelissen (21) showed that the action of dibenzoyl peroxide on carbon tetrachloride yields chlorobenzene, and a similar reaction has been observed by Reynhart (124) using tetrachloroethylene.

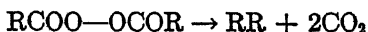
A remarkable correspondence between the reactions of the diacyl peroxides and the diazonium compounds formed the subject of a communication of Gelissen and Hermans (44), who suggested that an addition compound was formed between the peroxide and the hydrocarbon, which then decomposed with evolution of carbon dioxide. This mechanism is similar to that proposed by Hantzsch (see p. 176) for the decomposition reactions of diazonium salts with evolution of nitrogen. The reactions were represented thus:



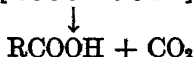
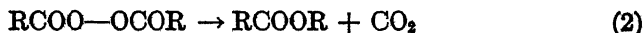
Examples are quoted in which the compound R'H may be a hydrocarbon, an alcohol, or water. It may be noted that several cases are known in which a diazonium salt decomposes in water with replacement of the diazo group by hydrogen without recourse to the use of a reducing agent (168, 101, 112). Further, Gomberg and Pernert (58) have drawn special attention to examples of the replacement of the diazo group by hydrogen in the

reactions of the diazo hydroxides, where the addition of a reducing agent is not necessary. These reactions show a close correspondence to the reactions of nitrosoacetanilide with aliphatic hydrogen-containing solvents recently carried out by Waters (153) and described in section VI.

In summarizing the reactions of the diacyl peroxides Gelissen and Hermans (46) distinguished between the thermal decomposition, which takes place on heating above the melting point, and in which two molecules of carbon dioxide are evolved, thus:



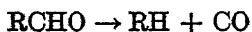
and the reaction with a solvent  $\text{R'H}$ , in which only one molecule of carbon dioxide is evolved, but which could proceed in two ways as shown above. The formation of biphenyl on the thermal decomposition of dibenzoyl peroxide, however, takes place only to a limited extent unless a catalyst is present (40) or unless a high temperature is used (123). Biphenyl is also formed by the action of ultra-violet light on dibenzoyl peroxide (35). In more recent surveys of the problem by Böeseken and Hermans (22) and by Hermans (76), the reactions of the diacyl peroxides have been represented in a new manner. It is held that when heated, either alone or with a solvent, they react according to one or more of the following equations:



Reactions 1 and 2 represent the main courses followed on thermal decomposition, whereas the reaction with a solvent,  $\text{R'H}$ , is now represented as a type of "double decomposition" (reactions 4 and 5), as the result of which two new peroxides are formed, each of which is capable of subsequent reactions as represented in the equations 1 to 5.

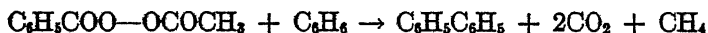
Although this scheme embraces in an apparently satisfactory manner the great variety of products which may be formed when a diacyl peroxide undergoes decomposition alone or in solution, yet it is difficult to find direct evidence to support the "double decomposition" reactions (4 and 5), which in many cases imply the formation, from a thermally unstable compound, of a new compound of similar constitution yet less stable. The

participation of free radicals in these reactions is not considered by Böese-ken and Hermans to be an essential feature, and the implication is drawn that the formation of free radicals is improbable. Reynhart (123) also considers the formation of free phenyl radicals in the thermal decomposition of dibenzoyl peroxide improbable, since when the decomposition was carried out in an atmosphere of bromine at 210°C. no bromobenzene was formed; similarly in the presence of iodine no iodobenzene was formed. This evidence, however, is not conclusive, for in an analogous reaction, the photochemical decomposition of aldehydes (compare p. 173), there is no mixed product, i.e.,

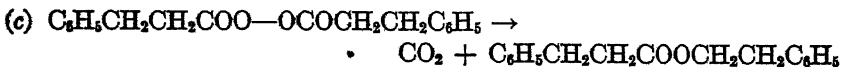
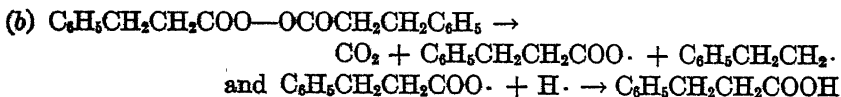
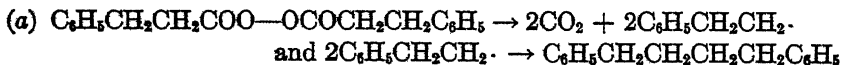


only, for the two free radicals, produced in close proximity, unite at once, before any other molecule can intervene (110, 6).

An extensive investigation into the reactions of the diacyl peroxides was also made by Wieland and Razubaiev (163), which included the reactions of many unsymmetrical diacyl peroxides,  $RCOO-OCOR'$ . With aromatic peroxides of the type  $C_6H_5COO-OCOC_6H_4R$  decomposition in benzene solution gave rise to two biaryls, namely  $C_6H_5C_6H_5$  and  $p-C_6H_5C_6H_4R$ , whereas in the case of benzoyl acetyl peroxide, biphenyl and methane were produced in addition to benzoic and acetic acids:



The fate of the acetate radical in this reaction resembles closely that of the acetate radical in the reactions of nitrosoacetanilide. Wieland, Schapiro, and Metzger (165) extended the investigations to include the thermal decomposition of a number of new symmetrical and unsymmetrical diacyl peroxides. In the thermal decomposition of dihydrocin-namoyl peroxide, diluted with sand, at 70°C. approximately 1.5 moles of carbon dioxide were evolved and the main reactions were represented thus:

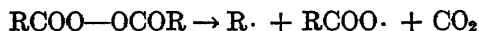


The greater part of the reaction proceeds according to equation *a*, but it is pointed out that the subsequent changes in the radical  $C_6H_5CH_2CH_2\cdot$  are not completely disclosed. Both 1,4-diphenylbutane and ethylbenzene were isolated, but no styrene was found. The source of the hydrogen in reaction *b* is not revealed. To account for the minor reactions which occur with the formation of ethylbenzene and compounds of higher molecular weight, it is held that the 1,4-diphenylbutane first formed may then react with more unchanged peroxide, as in the decomposition reactions carried out in solution. It is stated, however, that in none of these reactions is it necessary to assume the intermediate formation of free radicals, and that the reaction in solution is more likely to be one between peroxide molecules and solvent molecules. In the case of mixed aliphatic-aromatic peroxides it was established that it is the aliphatically bound carbon dioxide which is eliminated to a preponderating extent. A further example studied was the thermal decomposition of benzoyl *o*-chlorobenzoyl peroxide. It was argued that if free aryl radicals were formed the product should contain, not only 2-chlorobiphenyl, but also biphenyl itself and 2,2'-dichlorobiphenyl. No biphenyl was detected in the product, however. Against this argument must be brought the evidence from the thermal decomposition of phenylazotriphenylmethane, in which case the formation of a phenyl radical is highly probable, yet no biphenyl is formed.

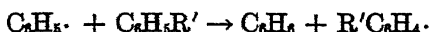
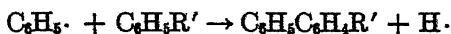
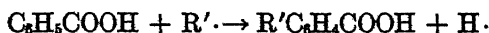
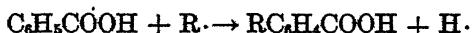
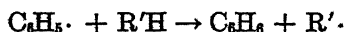
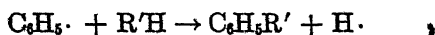
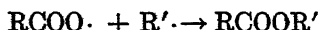
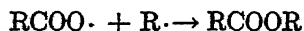
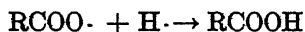
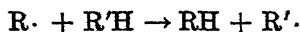
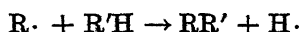
Wieland and his coworkers regard the correspondence between the reactions of the diacyl peroxides and those of the arylazotriarylmethanes, both with and without solvents, as superficial only. The difference, it is claimed, is illustrated best in the thermal decomposition in absence of solvent, for while phenylazotriphenylmethane yields some benzene and no biphenyl, dibenzoyl peroxide yields biphenyl and no benzene. This argument is, however, discounted, since Erlenmeyer and Schoenauer (32) have shown that benzene is formed when dibenzoyl peroxide suffers decomposition. There is also an important difference between the two cases, since in the phenylazotriphenylmethane molecule there is only one phenyl group, whereas in the dibenzoyl peroxide molecule there are two. The life of the free aryl radical is essentially very short and biphenyl formation, as opposed to benzene formation, is therefore likely to be far more probable in the case of the peroxide reaction in which the two free phenyl radicals would probably be produced simultaneously and in close proximity by the elimination of carbon dioxide from the symmetrical starting product. The decomposition of the diacyl peroxides seems to bear a similar relationship to the decomposition of the arylazotriarylmethanes as does the photochemical decomposition of aldehydes to that of ketones. It is a difference of degree rather than of kind.

The remarkable correspondence now revealed between the reactions of

the diazo hydroxides, the nitrosoacylarylamines, the arylazotriaryl-methanes, and the diacyl peroxides demands that the possibility of the participation of free radicals in the reactions of the latter class of compounds should be reconsidered. The available evidence points strongly to a specific reaction mechanism common to all four cases. The various reactions which the diacyl peroxides can undergo, both on thermal decomposition alone and on decomposition in solution, can all be accounted for satisfactorily by the initial formation of free radicals thus:



The free radicals thus produced, by further action with themselves or with other molecules, can then give rise to the various hydrocarbons, acids, and esters which are formed. Thus:



The intermediate formation of new unstable diacyl and acyl formyl peroxides by double decomposition, as assumed by Böeseken and Hermans (22), is no longer required.

More recently the thermal and photochemical decomposition of diacetyl peroxide in solution has been studied by Walker and Wild (150a), who have shown (a) that the reaction in solution is complex, (b) that in an excess of solvent (toluene) the thermal reaction is of the first order with respect to diacetyl peroxide, and (c) that in the decomposition in solution (cyclohexane or ethyl alcohol) less ethane and more methane is obtained than from the photodecomposition in absence of a solvent. Hence Walker and

Wild suggest that the primary process may consist of a dissociation into free acetate radicals, which decompose further into carbon dioxide and methyl radicals, which could combine together to form ethane or react with surrounding solvent molecules to give methane. These results again are in complete agreement with the properties of free radicals in solution as presented in this review.

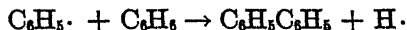
#### IX. PROPERTIES OF FREE ARYL RADICALS

Although it has been shown above that the arguments brought by Wieland and others, which tend to weigh against a free radical mechanism, are not insuperable, it should be emphasized that all the reactions of the diacyl peroxides may not involve the formation of free radicals. The same proviso must be applied to the reactions of the azo and diazo compounds.

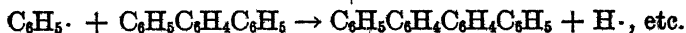
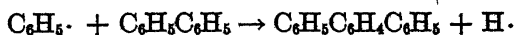
The free radicals can at most have only a transient existence and one can only postulate their production in thermal or photochemical self-decompositions, or in reactions of the same type occurring in neutral non-ionizing solvents.

The marked differences between the reactions of the free substances in the vapor phase and their reactions in solvents have already been stressed, and it has been pointed out that in the latter reactions the free radical invariably reacts with the solvent molecule. This indeed is a marked characteristic of the phenyl radical.

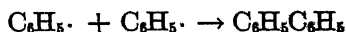
In opposition to the views set forth above, it might be contended that in every case some polymerization should be evident with formation of biphenyl, quite irrespective of the nature and presence of any second component or solvent. It is known that free phenyl radicals formed in the gaseous phase at relatively high temperatures and low pressures, as, for example, in the thermal decomposition of lead tetraphenyl (30) or from the action of sodium vapor on bromobenzene (79) give rise to biphenyl. In the reactions carried out in solution, however, polymerization to biphenyl does *not* take place (162, 157). Biphenyl formation only occurs when benzene is present,



and the isolation of ter-, quater- and even quinque-phenyl in smaller quantities, which is characteristic of these reactions, also indicates a reaction between the radical and a hydrocarbon molecule,



rather than reaction between two phenyl radicals, which can result in the formation of the binuclear hydrocarbon only,



The formation of a substituted diphenyl  $C_6H_5C_6H_4R$ , when reaction is carried out in a benzene derivative,  $C_6H_5R$ , also illustrates the same point.

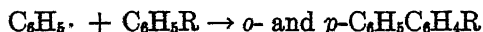
Thus, the main characteristics of the phenyl radical, when formed in the presence of a solvent, may be summarized as follows: (1) The free phenyl radical is an extremely reactive substance of short life, able to interact with and decompose almost the first molecule of any type which it encounters. (2) Polymerization to biphenyl is not encountered. (3) Reaction with non-aromatic hydrogen-containing solvents gives rise to the formation of benzene:



(4) Reaction with non-aromatic halogen-containing solvents gives rise to the formation of halogeno-benzene:



(5) Reaction with neutral aromatic liquids gives rise to the formation of biphenyl derivatives, in which the radical enters the nucleus at the ortho- and para-positions, irrespective of the nature of any so-called directing group which may be present:



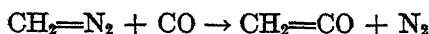
These properties are entirely consistent with those of the free alkyl radicals. Thus the free methyl radical will abstract hydrogen from practically any other organic molecule with formation of methane (129),



in both the gaseous and liquid phases (compare section III).

#### X. DIRADICALS

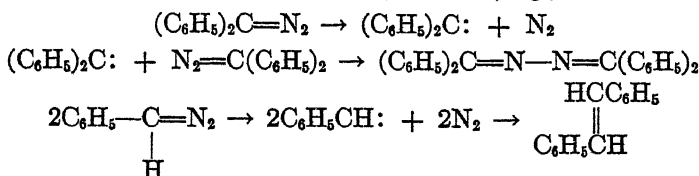
Just as azomethane on heating gives nitrogen and free methyl radicals, so diazomethane,  $CH_2=N_2$ , decomposes into nitrogen and the free methylene radical  $CH_2\cdot$  at a temperature of 350–600°C. The latter was conclusively identified by its reaction with tellurium, when telluro-formaldehyde,  $(CH_2Te)_n$ , was produced (127). As long ago as 1912, however, Staudinger and Kupfer (146) had shown that on heating in carbon monoxide diazomethane yielded a little ketene:



and suggested that free methylene was a transient product.

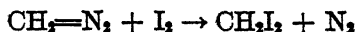
In 1916 Staudinger put forward the view that free divalent radicals were possible initial decomposition products of all aliphatic diazenes (aliphatic diazo compounds) (142, 143, 144, 145). On standing alone, or in inert sol-

vents such as ether or hydrocarbons, diazenes gradually evolve nitrogen and a ketazine is produced or, in a few cases, an olefin, e.g.,

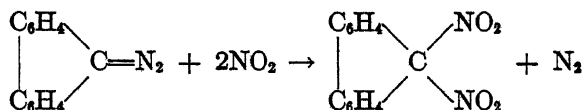


This reaction is promoted by ultra-violet light and is catalyzed by both iodine and oxygen.

Iodine itself reacts as follows:



and, as Wieland and Reisenegger (164) showed, nitrogen peroxide can replace the nitrogen by two  $\text{NO}_2$  groups, as, for example, in diazofluorene:

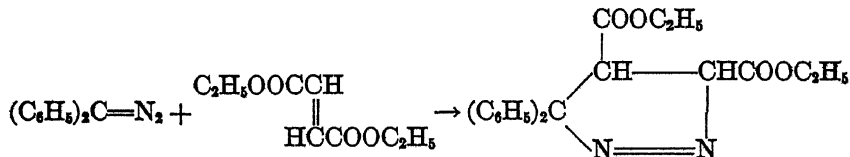


These reactions are reminiscent of those of triphenylmethyl and afford strong support to the hypothesis of fission into a neutral free diradical.

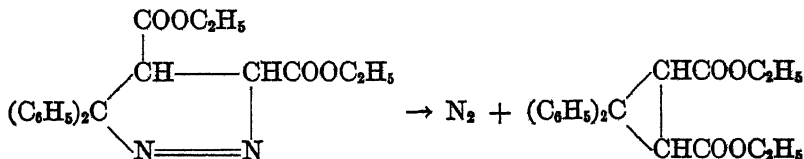
Fission of nitrogen also occurs, however, when aliphatic diazenes interact with polar reagents such as alcohols, acids, bases, and acyl halides, and it has been suggested that in these cases the nitrogen elimination follows a polar addition process, which yields a transient aliphatic diazonium ion (26):



With olefins undoubtedly an addition reaction occurs initially, for pyrazole ring compounds can easily be isolated:



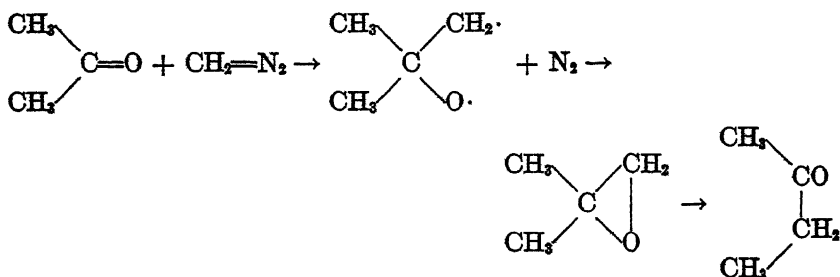
On heating, however, these cyclic azo compounds invariably lose nitrogen and give trimethylene ring derivatives.





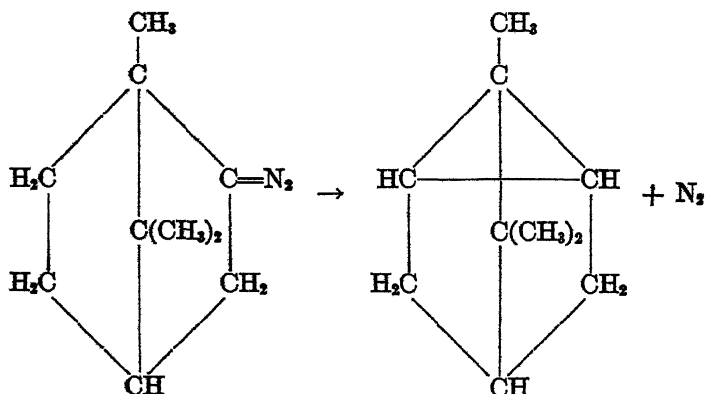
This final decomposition may well give rise to transient free radicals, just as in the case of the azo compounds considered in section IV. In some cases it takes place spontaneously, but in others heating alone, or in an inert solvent, is needed.

Similar circumstances have been recorded for the Schlotterbeck reaction between diazomethane and acetone (138, 2). Meerwein (98, 99) represents this reaction as follows:



and has established the fact that dimethylethylene oxide is an intermediate product. However, whilst Meerwein and also Mosettig and Burger (104) favor the free radical mechanism as depicted above, Robinson and Smith (132) consider that the whole process is polar in type.

The decomposition of diazocamphane (100) is another reaction which is possibly of non-ionic type; it yields tricyclene and not bornylene or camphene, which are products of ionic changes. Thus:



The decomposition of diazocamphor is similar.

In a very similar manner the azides may possibly yield a diradical with univalent nitrogen. Thus when phenyl azide is heated in benzene in a sealed tube at 150–160°C. azobenzene is produced (9, 10).



With *p*-xylene, however, the free radical,  $\text{C}_6\text{H}_5\text{N}\cdot$ , reacts to give *p,p'*-ditolyethane and aniline, the free radical thus reacting with an aliphatic side chain in the usual manner by abstracting hydrogen:

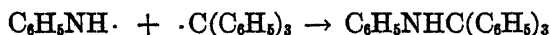


Schmidt (140) also suggested that hydrazoic acid yields the radical  $\text{HN}\cdot$ : when treated with sulfuric acid:

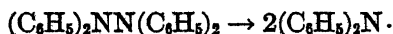


Goldschmidt and his coworkers (51, 52, 53) have suggested that the free radical  $\text{C}_6\text{H}_5\text{N}\cdot$  is also produced when phenyldichloroamine,  $\text{C}_6\text{H}_5\text{NCl}_2$ , decomposes, or when aniline is oxidized in non-ionizing solvents. Further, Goldschmidt and Wurzschnitt (52) oxidized aniline with lead peroxide, in dry ether containing hexaphenylethane, using anhydrous sodium sulfate to remove the water as it was produced, and obtained anilinetriphenylmethane in good yield.

They represent the reaction as follows:

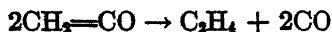


Evidence for the existence of the analogous free radical diphenyl nitrogen,  $(\text{C}_6\text{H}_5)_2\text{N}\cdot$ , which is produced by the dissociation of tetraphenylhydrazine,



just as hexaphenylethane dissociates into triphenylmethyl, has been brought forward by Wieland (154, 161, 155), but its participation in certain reactions of the tetraarylhydrazines is regarded as unlikely (156).

The carbonyl compounds analogous to the aliphatic diazenes are the ketenes, and these substances will, on heating to a high temperature, eliminate carbon monoxide (compare the reactions of the ketones, section III):



The most characteristic properties of the ketenes are their additive reactions, which take place at a double bond (141). It has been suggested, therefore that the ketenes might be regarded as diradicals (160, 81).

## XI. ELECTRODE REACTIONS

A neutral radical must obviously be produced whenever an ion is discharged at an electrode, but the liberated radicals then promptly react

either with each other or with other adjacent ions or neutral molecules. Thus in the electrolysis of dilute sulfuric acid there occurs:

at the cathode: (i)  $\text{H}^+ + e \rightarrow \text{H}\cdot$

(ii)  $2\text{H}\cdot \rightarrow \text{H}_2$

at the anode: (i)  $\text{OH}^- \rightarrow \cdot\text{OH} + e$

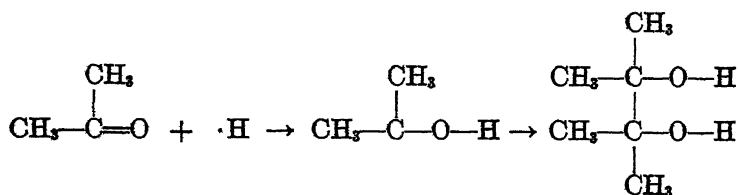
(ii)  $2 \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$

(iii)  $2 \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{O} \quad (\rightarrow \text{O}_2)$

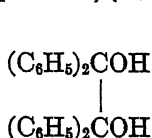
Hence free neutral radicals may be involved in many of the electrolytic reactions that are used in practical organic chemistry. However, an exact study of each reaction is required before its precise mechanism can be established, for it has been shown that many reactions which were once formulated as unions of ions upon discharge are in reality much more complicated, and involve purely chemical reactions brought about by reactive molecular products (such as hydrogen peroxide) formed in the immediate vicinity of the electrode (50).

#### A. Cathode reactions

A wide range of organic compounds can be reduced, either in acid or in alkaline solution, if placed in the cathode compartment of an electrolytic cell; the nature and yield of the reaction product depend mainly upon the electrode potential and the current density employed. The reduction of all covalent organic compounds at a cathode is of course brought about by the hydrogen liberated at the electrode, but it is rarely possible to decide whether it is the initially produced hydrogen atoms or the hydrogen molecules which attack the organic compound. The reduction of an organic compound at a metallic cathode may be catalyzed by the electrode, and metals are powerful catalysts for reduction by hydrogen gas. A few of the experimental observations of electrolytic reduction, however, are explicable most easily upon the free radical hypothesis. By the electrolytic reduction of ketones, pinacones are produced, whilst aldehydes can yield glycols (166, 148, 136). Pinacone (pinacol) formation can be explained most simply as due to combination of two free ketyl radicals:



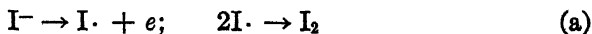
In the same way sodium benzophenone,  $(\text{C}_6\text{H}_5)_2\text{CONa}$ , yields benzopinacol,



on treatment with water. This hypothesis receives further confirmation from the fact that, in warm acid solutions, ketones on electrolysis at mercury cathodes yield mercury dialkyls, and at lead cathodes, lead tetraalkyls (147, 149, 122, 134, 63).

### B. Anode reactions

Many inorganic anode reactions have been considered to involve a combination reaction of free neutral radicals, e.g.,

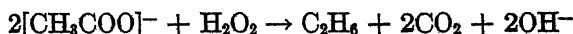


It has been demonstrated that when solutions of zinc ethyl or of ethyl magnesium bromide are electrolyzed the free ethyl radical is liberated at the anode (73, 91, 92). If this is composed of a metal like lead, antimony, or bismuth, it is attacked with formation of the corresponding organo-metallic compound. At an inert electrode a mixture of hydrocarbon gases is liberated.

Kolbe's reaction, the formation of carbon dioxide and a hydrocarbon upon electrolysis of a salt of an aliphatic acid, was represented by Crum Brown and Walker (29) as follows:



On the other hand Fichter and his coworkers (34, 33, 36) considered that an organic peroxide or per acid was first formed at the anode, and that this, like any other organic peroxide, then decomposed to give carbon dioxide and a mixture of hydrocarbons. From a detailed investigation of the electrolysis of acetates, however, Glasstone and Hickling (49, 50) have come to the conclusion that in aqueous solution the acetate anion is not discharged to any appreciable extent, but that hydroxyl anions are discharged preferentially, and unite in pairs to form hydrogen peroxide. The hydrogen peroxide, formed in high local concentration and in the presence of a catalyst (the electrode material), is then presumably able to oxidize acetate anions to ethane and carbon dioxide.

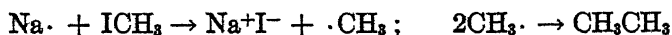


This oxidation possibly takes place with the intermediate formation of diacetyl peroxide. In non-aqueous solutions, such as glacial acetic acid,

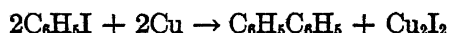
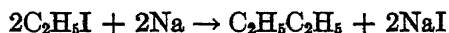
in which hydrogen peroxide cannot be formed, the acetate anions may be discharged, and under these circumstances the mechanism of Crum Brown and Walker would be valid.

## XII. FREE RADICALS FROM REACTIONS INVOLVING METALS

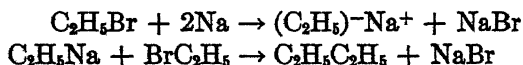
Polanyi and his coworkers have shown that in the vapor phase atoms of the alkali metals can undoubtedly decompose alkyl halides with production of free radicals (see section I),



but it is doubtful whether this same mechanism can be applied to the hydrocarbon syntheses of Fittig, Wurtz, and Ullmann, which are usually carried out in inert solvents: e.g.,

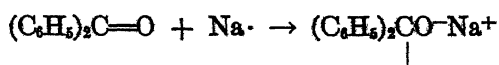
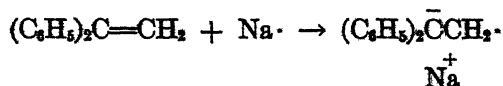


since the reactions may proceed instead by means of the formation of organometallic compounds, e.g.,

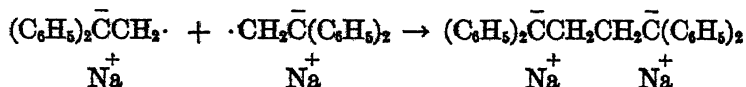


and evidence can be adduced in support of each theory (167, 3, 139, 169, 173, 103).

Transient free radicals may also be produced at one end of a double linkage when an alkali metal atom adds on to the other end, e.g.,

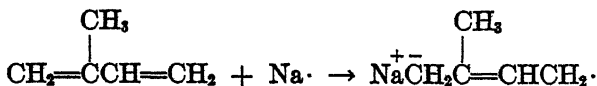


These free radicals promptly unite to form double molecules (137), e.g.,

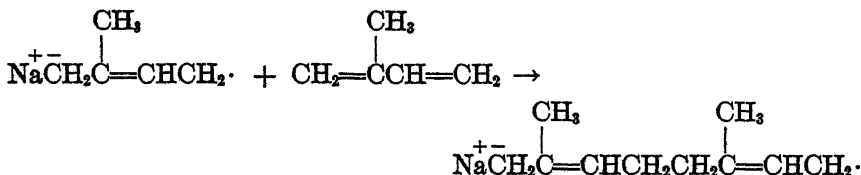


but a chain polymerization process may also be initiated (8) and in this way one can explain in a simple manner the action of sodium metal in catalyzing the chain polymerization of styrene, isoprene, and analogous substances, though here again the mechanism of the reaction is not

without doubt (1, 170, 171, 172). For example, if sodium metal adds on to isoprene as follows



there would be produced a free radical which could unite with a second isoprene molecule to produce a dimeric free radical:

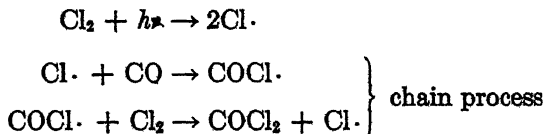


and by continuing this process a long-chain polymer might be formed.

Free radical formation may also explain the process of polymerization of these substances by ultra-violet light (38). It is also of interest to point out that the organic peroxides, such as dibenzoyl peroxide, are frequently employed as catalysts in bringing about the chain polymerization of olefins. From a consideration of the properties of these compounds (see section VIII), it can be seen that quite possibly they act by initiating free radical formation. In this connection too it may be mentioned that both in the gaseous phase (150) and in the liquid phase under high pressure (28, 131) it has been shown that the free methyl and ethyl radicals react with ethylene to form a hydrocarbon oil of high molecular weight.

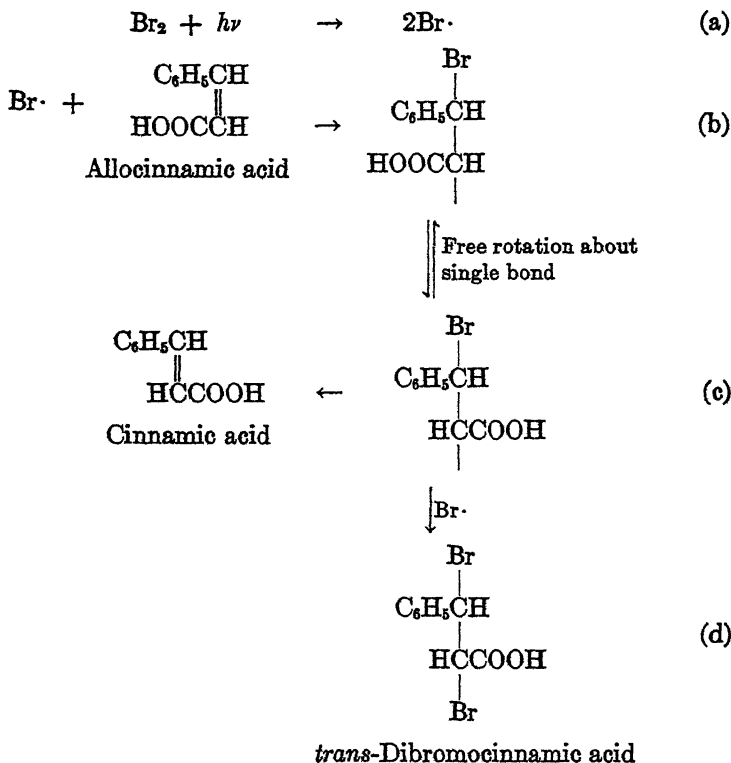
### XIII. REACTIONS DUE TO FREE HALOGEN ATOMS

It is well known that halogen molecules are decomposed into neutral atoms by exposure to ultra-violet light, and many photochemical chain reactions of chlorine and bromine vapors are now believed to occur in consequence of the formation of these atoms. Thus the formation of phosgene is represented as follows (17, 19, 18):



Berthoud (11, 13, 14, 15, 12, 16) and his colleagues have shown that the photochemical reactions between bromine and olefins in non-ionizing solvents are also due to the initial production of halogen atoms, since, with feeble illumination, the rate of reaction is proportional to the square root of the intensity of the light, indicating that each bromine molecule is split

up into two reactive bromine atoms. The photochemical reactions between allocinnamic acid and bromine can thus be represented as follows:



In connection with this atomic mechanism for addition to olefins, recent observations of Kharasch and his coworkers (87, 88, 89, 85, 86) are of considerable interest. These investigators have shown that a pure olefin adds hydrogen bromide in the manner predicted by Markownikow's rule: e.g.,



If the olefin has been exposed to the air, however, the hydrogen bromide tends to add on in the reverse manner:



This change is due to the presence of peroxides, and the addition of a little dibenzoyl peroxide to an olefin may completely reverse the mode of addition of hydrogen bromide from the normal type (a) to its converse (b). Since peroxides can be regarded as possible generators of neutral

radicals it may be suggested that the addition process (b) is one requiring the transient production of neutral atoms of hydrogen and bromine from the hydrogen bromide.

After the manuscript of this review had been submitted for publication, Kharasch, Mansfield, and Mayo (86a) published a short communication in which they have put forward the same point of view as that given immediately above. In support of this theory they have shown that (*cis*)-isostilbene is not converted into (*trans*)-stilbene by the catalytic action of hydrogen bromide in the dark except in the presence of air or peroxidic substances, when the reaction becomes very rapid. The reaction initiated by peroxides is thus of exactly the same type as are the photochemical reactions of Berthoud. More recently still, Kharasch, Margolis, White, and Mayo (86b) have further extended the theory of reaction by atomic bromine in presence of peroxides to the halogenation of aromatic side chains in a way which had been very tentatively foreshadowed by Waters (152a). It has been shown that whereas the nuclear substitution of toluene is not catalyzed by peroxides, substitution in the side chain is very markedly affected. Thus when toluene is brominated in the dark at 25°C. in the presence of ascaridole, the reaction takes half an hour and the product is over 98 per cent benzyl bromide.

The peroxide effect discovered by Kharasch may be taken as an indication that olefins form addition compounds with neutral radicals, for oxygen gas is a paramagnetic molecule, which must therefore contain two uncoupled electrons and may be represented as a diradical  $\cdot\text{O}-\text{O}\cdot$ . It is beyond the scope of this review to discuss the reactions of oxygen gas, but it may be mentioned that Haber and Willstätter (62) have suggested that free radicals intervene in a large number of oxidation processes. The subject has been summarized recently by Rice and Rice (130) and is still speculative, for as yet no experimental evidence has been produced indicative of the independent existence of neutral radicals in any oxidation process.

#### XIV. CONCLUSIONS AND SUMMARY

The foregoing sections show that strong experimental evidence is available at the present time to substantiate the general statement made in the introduction to this review, that free neutral radicals may be formed by thermal or photochemical decompositions of organic molecules in the liquid phase as well as in the gaseous phase, and that these neutral radicals, when formed, have the properties of free atoms, or of the neutral entities discharged at electrodes in many electrolytic processes. It has been amply demonstrated, moreover, that the free neutral radicals are exceedingly reactive substances, and can therefore have only a transient existence.



So very reactive are they that they interact with and decompose practically the first molecule that they encounter, and, in consequence, the reactions which involve free radicals in solutions are almost without exception reactions between free radicals and solvent molecules. No solvent has yet been discovered which is inert to these free neutral radicals, and in this way the latter entities may be differentiated from free charged ions, which are often stable in solution.

The great reactivity of free neutral radicals, however, makes their experimental detection exceedingly difficult, and without the indubitable evidence of free radical reactions in the gaseous phase the analogous reactions in solution would have received but uncertain recognition.

The authors are well aware that the interpretation of the experimental evidence which they have set forward in this review may, in some cases, be open to criticism on theoretical grounds, for but few of the researches have yielded decisive results in themselves, although they accord with the general viewpoint which has been set forth. There may exist also several other reactions in organic chemistry in which transient free neutral radicals intervene, but it has been felt that, when the available experimental evidence is but fragmentary, theoretical speculation cannot be justified.

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# A SYMPOSIUM ON GASEOUS COMBUSTION<sup>1</sup>

## INTRODUCTION TO THE SYMPOSIUM. THE DEVELOPMENT OF COMBUSTION RESEARCH AND THE PRESENT OUTLOOK<sup>2</sup>

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Nine years ago the Division of Gas and Fuel Chemistry of the American Chemical Society, jointly with the Division of Petroleum Chemistry, sponsored a symposium which was essentially on gaseous combustion.<sup>4</sup> The present symposium reflects the progress in combustion research made since then. Three divisions may be distinguished in this research. One includes the chemistry and kinetics of slow and explosive oxidation reactions. Another is the propagation of flame with the establishment of boundaries between burnt and unburnt gases. A third consists of a study of the state of the burnt gas, that is, the establishment of thermodynamic equilibrium and temperature gradients. In a number of technical problems such as are presented by internal-combustion engines, problems in more than one of these divisions occur.

The time limitations that are unavoidably placed on the present large program and other circumstances have prevented the inclusion of contributions from many active investigators both here and abroad. It is regretted that it was not possible to obtain a representative group of contributions in the exceedingly important and active field of catalytic com-

<sup>1</sup> This symposium was held by the Division of Gas and Fuel Chemistry, with the cooperation of the Divisions of Industrial and Engineering Chemistry, Petroleum Chemistry, and Physical and Inorganic Chemistry, at the Ninety-fourth Meeting of the American Chemical Society, Rochester, New York, September 9-10, 1937.

<sup>2</sup> Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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<sup>4</sup> This symposium was held at the Seventy-sixth Meeting of the American Chemical Society, held at Swampscott, Massachusetts, September 10-14, 1937. The papers of this symposium were published in *Industrial and Engineering Chemistry*, Vol. 20, pp. 998-1057 (1928).

bustion. The problem of the diffusion flame was ably treated at the earlier symposium, and it has been omitted from this one since little could be added at this time that would contribute to a further understanding of the subject. The subject of the detonation wave, which in the main is a physical problem in hydrodynamics, has also been omitted, since it had already reached an advanced stage of theoretical development. Some more recent discoveries in this field, such as the discontinuous progress of the detonation wave and the spinning detonation in which a spiral track is described by the wave front, merit further study. It does not appear that problems of technical interest are involved.

Certain fundamental lines of development are indicated by the present accomplishments in the various divisions of the symposium. Ultimately, it is desired to understand fully the intricate chemistry and kinetics of the oxidation of combustibles. In the case of hydrogen we are probably not very far from this realization. This can also soon be said of carbon monoxide. The reactions of hydrocarbons are much more complicated. There is a well-founded suspicion that the key to the chemistry and kinetics of hydrocarbon oxidation lies in the formation and decomposition of peroxidic substances. The subject of the complicated and extremely important heterogeneous reactions of hydrocarbons is a field of study in itself. It can be stated with some assurance that there is hardly a case of slow oxidation or of the establishment of a critical condition leading to ignition, as, for example, in engine knock, that does not involve surface reactions of some kind. The function of the interface between gas and fuel droplets as the possible initiator of ignition in the Diesel engine should not be overlooked and deserves study. Thus, the oxidation of organic substances offers challenging problems to the kineticist. Such studies should stimulate research and technical development in many directions, possibly much more than we can foresee now.

There are a number of problems encountered that are of such extreme complexity that a rational and immediate scientific solution seems to be quite impossible. Sometimes they are of such practical importance that something has to be done about it, despite the impossibility of a quantitative scientific analysis of the problem or even of the guiding principles that are involved. A perplexing problem of this sort is that of fuel rating. Nevertheless, one must admire the practical progress that has been made in this work. It is in the nature of the problem that the methods of rating fuels developed thus far are not entirely satisfactory, and that their shortcomings become more pronounced as the limits of tolerance in fuel specifications narrow. If active investigators in this field were asked today whether they could improve on the principles of present fuel rating practice, the answer would probably be in the negative. They would

protest that they have not even an assured qualitative knowledge of the processes that occur between the fuel, the air, and the surface in the engine; much less could they give a quantitative estimate of the likelihood of knock in the Otto engine or of the length of the preignition period in the Diesel engine. There is, however, nothing to suggest that the problems are insoluble.

Among other problems of great complexity are those of ignition by a local source such as a spark and of the propagation of flame. In the approach to both problems the older idea that only the transfer of heat need be considered the decisive element must now give way to the inclusion of the migration of chain carriers and the various kinetic aspects of chain development. There will be presented in this symposium pertinent experiments pointing to the rôle of chain carriers, and also a first attempt at a mathematical analysis of the dual problem of heat flow and diffusion of chain carriers. In safety practice the specification of an admissible spark would be materially aided by a deeper understanding of the action of the spark on a combustible mixture. A similar situation exists with respect to the problem of flame propagation which entails limits of inflammability, the latter being of utmost practical importance in hazardous industrial operations.

Whether mine and other explosions can be effectively inhibited by some means such as the addition of small amounts of substances acting as negative catalysts to the reaction chain development, remains to be answered in the future. However, there is no question but that present knowledge can materially aid in the elimination of thousands of explosion hazards that today lurk below and above ground all over the country.

A much clearer description of the state of the burnt gas that emerges from the flame can now be given than was possible ten years ago. The essential tool to study the burnt gas has been provided by band spectroscopy, in the form of accurate data of energy contents (specific heats) and equilibrium constants. It has become possible to establish order in this field, which has admittedly been in a confused state ever since it was first touched upon by Bunsen. It has been shown that the flame effects a potent transformation of the combustible mixture to practically thermodynamic equilibrium, leaving no room for large hidden sources of energy in the form of latent heat. There are, however, certain problems that should be studied further, such as the anomalous effects that appear as a time-dependence of specific heats and the study of flames of very rich mixtures of organic combustibles where complicated and partly unknown dissociation equilibria exist.

No doubt we all shall learn and profit from the present gathering. It is hoped that the impetus given by the work presented will stimulate further research along both experimental and theoretical lines.





## CHEMICAL ACTION IN THE GLOW DISCHARGE. XV

### REACTIONS PRECEDING IGNITION

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Unusual opportunities for the study of the factors underlying ignition are offered by the glow discharge, since within the discharge are to be found positive ions, atoms, excited molecules, and electrons of known energy content. All of these are present under conditions fairly well known and controllable by the investigator.

The glow discharge may be produced in a cold electrode tube at pressures ranging from a hundredth of a millimeter to several centimeters. The discharge itself consists of the Crookes dark space adjacent to the cathode, followed in order by the negative glow, the Faraday dark space, and the positive column which extends to the anode. Any of these regions, except the Crookes dark space, may be eliminated by moving the anode towards the cathode, without changing the characteristics of the remaining regions.

The potential drop across the Crookes dark space is 300 volts or more, depending on the conditions of the experiment, the actual gradient often being 1000 volts per centimeter. The length of the dark space is about one-half a mean free path between ionizing collisions for an electron of energy corresponding to the cathode potential drop. The potential drop in the negative glow is negligible. The length of the negative glow in various gases corresponds exactly to the range of electrons possessing an energy equal to the full cathode potential drop as given by Lehmann (4). This makes it possible to use directly the data of Lehmann in computing the number of positive ions formed per electron in the negative glow.

The Faraday dark space is a low energy region in which the electrons leaving the negative glow are accelerated until they reach the ionization potential of the gas, at which point the positive column sets in. The gradient in the Faraday dark space is usually of the order of 20 to 25 volts per centimeter. The positive column is a region of low energy ionization. The average energy of the electron is from 6 to 8 volts, indicating that the maximum energy does not materially exceed the ionization potential. The gradient is of the order of 15 to 20 volts per centimeter.

Chemical reactions which may be produced in the glow discharge are of two general types, propagating and non-propagating. Under controlled conditions it is possible to study the reaction in explosive mixtures without propagation. By varying the conditions of the experiment, reaction chains can be introduced to study the factors influencing the reaction through various degrees of propagation until ignition occurs.

A detailed description of the various reactions studied has been presented in a series of articles (1).

#### NON-PROPAGATING REACTIONS

Typical reactions studied under non-propagating conditions are the synthesis of ammonia, the oxidation of nitrogen, the formation of ozone, the oxidation of hydrogen, the oxidation of carbon monoxide, and the oxidation of methane. The decomposition of ammonia, nitrogen dioxide, nitrous oxide, water, methane, and carbon monoxide have also been studied. It should be pointed out that in these studies conditions were so arranged that only the forward reaction was in evidence; any possible back reaction was completely, or almost completely, eliminated from the experiment.

Since all these reactions as they occur in the discharge possess marked similarities in character, the various factors influencing the rate of reaction will be described for the entire series, rather than for individual cases.

##### *1. Portion of the discharge in which the reaction occurs*

The Crookes and Faraday dark spaces appear incapable of inducing reactions. All reactions occur readily in the negative glow except the synthesis of ozone, failure in this case being apparently due to the difficulty in eliminating the back reaction. Under no conditions has it been found possible to ignite explosive mixtures in the negative glow, although slight evidence of chains was observed at high current densities. In the positive column both propagating and non-propagating reactions may be produced; at low current densities chains are inappreciable even in the most explosive mixtures.

##### *2. Effect of pressure*

The rate of reaction in the negative glow is independent of the pressure over the range investigated (20 mm. to 0.2 mm.). The characteristics of the glow are difficult to control over a greater pressure range. The absence of a pressure effect shows the reactions to be of zero order. In consequence it is possible to state definitely that the reaction must be initiated by specific reaction centers, rather than by regions of high energy density. In addition it is evident that any state which is in equilibrium with

any other state does not participate in the reaction; thus the reaction  $A + B_2 \rightarrow AB_2$  will show a pressure coefficient if an  $A_2 \rightleftharpoons 2A$  equilibrium exists in the gas.

### 3. *Effect of current*

The rate of reaction is proportional to the current over as wide a range as can be studied. The immediate interpretation of this fact is that the reaction is initiated by specific reaction centers, formed presumably by direct electron impact. Interaction between these primary reactive states, or conditions involving the interaction of primary with other excited states formed in the discharge, can be eliminated from the reaction mechanism; likewise the formation of initial reactive centers by the interaction of non-reactive primary states can be excluded; all of these possibilities require the rate to be dependent on some higher power of the current.

The rate of production of positive ions in the discharge is known to be independent of the pressure, and proportional to the current over the region where the voltage remains constant. The intensity of the characteristic spectrum of the discharge indicates that the concentration of atoms and excited molecules is dependent on the pressure and the current density. Direct measurements of the atom concentration in the discharge by Crew and Hulburt (3) also confirm this contention. The natural conclusion to be drawn, therefore, is that the initial reaction centers are positive ions formed by direct electron impacts.

### 4. *Effect of temperature*

Reactions in the negative glow are unique in that they possess either a zero or a negative temperature coefficient. Even the oxidation of hydrogen occurs at the same rate over a 400°C. change in temperature. The complete absence of a positive temperature coefficient is of particular significance in this study of the nature of the initial reaction centers, since it shows that these centers contain within themselves all the energy necessary for reaction. Reaction occurs, therefore, between the original active centers and normal molecules.

### 5. *Effect of added gases*

In syntheses the rate of reaction is always accelerated by the addition of the reacting gas having the higher ionization potential, and retarded by addition of the gas with the lower potential. To illustrate: in the oxidation of hydrogen the rate for  $2H_2-O_2$  mixture is 6.5 molecules per electron of current, in an  $8H_2-O_2$  mixture it is 8.0 molecules per electron, while in an  $H_2-2O_2$  mixture it is only 3.5 molecules per electron.

Additions of foreign gases to combining mixtures, with the exception of

helium, retard the rate in proportion to the extent to which they absorb energy. Helium, with its high ionization potential of 24.5 volts, accelerates the rate up to a partial pressure of about 50 per cent. The general

TABLE 1  
*M/N ratios*

REACTION	$\frac{M}{e}$	$\frac{M}{N_T}$	$\frac{M}{N_R}$	<i>T</i> °C.
$N_2 + 3H_2 = 2NH_3$	0.82	$\frac{0.82}{8.0} = 0.1$	$\frac{M}{N_2^+} = \frac{0.82}{4.5} = 0.2$	-183
$NH_3 \rightarrow N_2 + 3H_2$	3.7	$\frac{3.7}{8.0} = 0.46$		+20
$N_2 + 2O_2 = 2NO_2$	0.92	$\frac{0.92}{7.8} = 0.12$	$\frac{M}{N_2^+} = \frac{0.92}{2.7} = 0.35$	-183
$2NO_2 \rightarrow N_2 + 2O_2$	20.0	$\frac{20}{13} = 1.55$		+170
	60.0	$\frac{60}{13} = 4.65$		+20
$2N_2O \rightarrow 2N_2 + O_2$	14.0	$\frac{14}{7} = 2.0$		+22
	14.0	$\frac{14}{7} = 2.0$		+500
$2H_2 + O_2 = 2H_2O$	6.5	$\frac{6.5}{10} = 0.65$	$\frac{M}{H_2^+} = \frac{6.5}{5} = 1.3$	-183
$2CO + O_2 = 2CO_2$	6.5	$\frac{6.5}{9} = 0.72$	$\frac{M}{CO^+} = \frac{6.5}{6.0} = 1.1$	-183
$CH_4 + 2O_2 = CO_2 + 2H_2O$	10.5	$\frac{10.5}{8.3} = 1.3$	$\frac{M}{CH^+} = \frac{10.5}{2.8} = 3.8$	-183
$2CH_4 \rightarrow C_2H_4 + 2H_2$	3.1	$\frac{3.1}{7.8} = 0.4$		-183

*M* in syntheses is the number of molecules formed; in decompositions the number decomposing.

*N<sub>T</sub>* is the total number of positive ions formed per electron of current.

*N<sub>R</sub>* is the number of positive ions of reactant having the higher ionization potential.

*e* denotes electrons of current in the outer circuit.

conclusion may be drawn, therefore, that ions of the reacting gas having the lower ionization potential and ions of inert gases, except helium, are relatively ineffectual in initiating reactivity.

In decompositions the addition of foreign gases may or may not retard the rate, depending on the specific nature of the reaction. In the decomposition of nitrous oxide the rate is decreased by foreign gases to the extent to which they reduce the number of  $\text{N}_2\text{O}^+$  ions as computed from the relative stopping power for electrons. The decomposition of nitrogen dioxide, on the other hand, is actuated by foreign ions almost as readily as by  $\text{NO}_2^+$  ions.

### 6. Comparative ion efficiency

Since the length of the negative glow is exactly equal to the range of electrons for corresponding voltages as given by Lehmann, it seems justifiable to use Lehmann's values for the number of electron volts required to produce an ion pair, in computing the number of positive ions formed per electron in the negative glow. In making the calculations the positive ion current to the cathode was neglected, since it represents only a small per cent of the total current (2). In cases where the number of electron volts required to produce one ion pair has not been determined by Lehmann, 45 was used as an average value.

In syntheses the number of molecules formed is used in the calculations, while in decompositions the number decomposed is considered.  $M$  refers to the number of the various molecules underlined. The  $M/N$  ratios are given in table 1 for both the total number of ions and for those ions having the higher ionization potential.

It is interesting to note that the  $M/N$  ratios computed above compare favorably with the values obtained by Lind with  $\alpha$ -rays (5). The conspicuous fact to observe is that the ratios are all small, and that in no instance is it necessary for the initial reaction center to collide with more than three molecules for the reaction to go to completion.

## PROPAGATION REACTIONS

The various factors which determine the reactivity in the discharge respond in an entirely different manner for propagation reactions from that described for initial reaction centers. Nevertheless, it is possible, by gradual changes in the experimental conditions, to follow the reaction from the initial zero-order type through various stages involving reaction chains until the ignition point is reached.

### 1. The effect of pressure, current, and temperature

The reactivity in the positive column for explosive mixtures exhibits a marked interdependence between pressure, current, and temperature. For each explosive mixture a combination of these three factors can be chosen below which the rate is of zero order, the reaction behaving exactly

as that in non-explosive mixtures. Above these particular conditions the rate increases nearly hyperbolically with pressure, more nearly exponentially with current, and moderately with temperature; in the hydrogen-oxygen reaction a 300°C. rise above room temperature increases the rate eightfold. Ignition occurs when the rate versus current, temperature, or pressure curve becomes asymptotic with the rate axis. Ignition can be induced in the positive column when the total expenditure of energy in this region is less than one two-hundredths of that being expended in the negative glow where the reaction is strictly zero order.

The rapid increase in rate with current suggests that energy states formed in the discharge other than those serving as initial reaction centers are involved in the chain mechanism. The positive temperature coefficient indicates that the reaction chains are favored by high thermal states in the gas. The pressure effect, as will be seen in the next paragraph, results largely from a retardation in the rate of diffusion of the various contributing energy centers out of the path of the reaction chain.

## *2. The effect of added gases*

The influence of added gases on the rate of reaction is in distinct contrast to that described for non-propagating reactions. The addition of various gases accelerates the rate to the extent to which diffusion is retarded. This is illustrated in the hydrogen-oxygen case in which hydrogen, helium, a mixture of hydrogen and oxygen ( $2\text{H}_2:\text{O}_2$ ), water vapor, argon, nitrogen, oxygen, and nitrous oxide enhance the rate, the effect increasing in the order named. These results indicate that high energy states are necessary for the maintenance of the reaction chains, or, conversely, that the chains will tend to break upon entering a region of normal energy density.

## MECHANISM OF REACTION

The results that have just been described make it possible to draw certain general conclusions concerning the reaction processes involved in the glow discharge; these conclusions are independent of any specific mechanism of reaction.

1. The reaction is induced by initial reaction centers. These centers are some energy-rich molecular state, and not regions of high energy density.

2. The initial reaction centers are formed only by primary processes occurring in the discharge, presumably by direct electron impact.

3. Non-propagating reactions occur when the reaction centers collide with normal molecules. Energy over and above that contained in the initial centers is unnecessary for the reaction.

4. Propagation occurs in explosive mixtures when the initial reaction

centers, or these centers associated with normal molecules, collide with energy-rich molecular states.

5. Processes which retard diffusion tend to enhance the effect of propagation, and to lower the energy input necessary for ignition.

Any detailed mechanism that may be suggested for the processes involved in the reaction about the active centers entails considerable speculation; in consequence an attempt to outline such a mechanism must be considered merely as a working hypothesis. It is definite, however, that any tenable mechanism must conform to the observed facts outlined above.

There is considerable evidence to suggest that the primary reaction centers are positive ions formed by direct electron impact in the discharge. The fact that the temperature coefficient is zero or negative for non-propagating reactions argues against the initial centers being atoms or excited molecules, since photochemical reactions which have been assigned to these states usually possess a positive temperature coefficient. Insofar as data are available the results indicate that the negative temperature coefficient for the rate can be correlated with the temperature coefficient for the dielectric constant of the gases present. Since the forces involved in the association of neutral molecules about an ion have been shown by Loeb (6) to be a direct function of the dielectric constant of the molecules, the apparent relationship between temperature and dielectric constant suggests some type of cluster mechanism.

The fact that propagation occurs in the positive column but not in the negative glow may result from one of two possibilities: Either some active state is formed in the positive column and not in the negative glow which gives rise to reaction chains, or else some condition exists in the negative glow and not in the positive column which is detrimental to chain formation. While the data are insufficient to determine which of these two possibilities is correct, it seems very doubtful that any active state can be produced in the positive column that is not formed in greater abundance in the negative glow. The zero-order conditions prevailing in the negative glow suggest that the life of the active centers in the gas phase is too short to permit the development of reaction chains.

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## THE MECHANISM OF IGNITION BY ELECTRIC DISCHARGES

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The precise sequence of events by which a potentially explosive gaseous mixture is caused to ignite has for long been a matter of speculation and experiment, and has suffered several reinterpretations in the light of various theories. Of the two commonest modes of ignition, electrical and thermal, the former, being inherently the more complex, has received the less attention. Its very complexity, however, insofar as it places a greater number of controllable variables at the disposal of the investigator, gives it added utility as a means of probing the molecular processes involved. This paper is intended briefly to survey the development of the theory of electrical ignition of explosive gaseous mixtures, and to give an account of its present position.

The general characteristics of electrical ignition can be briefly summarized: (1) *Limits of inflammability*. All combustible gases in admixture with air or oxygen have the property in common that explosion will only occur within certain limits of composition. In all cases which have been examined, more electrical energy is necessary to bring about ignition of mixtures near the limits than in the middle zone of the region of inflammability. In this respect electrical ignition differs markedly from thermal ignition. (2) *Limiting igniting pressure*. A given gaseous mixture becomes increasingly more difficult to ignite as its pressure is reduced, and a greater dissipation of electrical energy becomes necessary to initiate explosion. Hence the incendivities of different sparks may be compared by determining the least pressures at which they will ignite a given mixture. Such limiting pressures have only relative significance; up to the present time no absolute lower pressure limit for electrical ignition has been established. (3) *Least igniting energy*. Alternatively, the relative ignitabilities of different gas mixtures may be compared by measuring the least sparks which will ignite them. The igniting spark may be characterized, for example, by its total energy.

A bibliography of published work is appended to this paper. Because of imperfect control of electrical factors, much of the earlier work on electrical ignition cannot be used as a sound basis for generalization; indeed, progress has to a large extent been conditioned by improved control and

understanding of the electrical factors underlying the phenomena. The development of early ideas may be briefly outlined.

The alternative possibilities that ignition might be the result either of specifically electrical effects or of thermal effects due to the conversion of electrical energy to heat energy have been recognized from the time of the first systematic work on the subject. Coward and his collaborators (9, 8) determined the sensitivities of various gaseous mixtures by the method of limiting igniting pressures. Certain diluents (e.g., oxygen up to 70 per cent) were found to decrease the limiting (to certain arbitrary spark conditions) igniting pressures of hydrogen-oxygen mixtures, whilst others brought about an increase; a partial correlation appeared to exist between ignitability and thermal conductivity. Hence the view was taken that thermal factors were predominant, although it was necessary to make an exception in the case of carbon monoxide-oxygen mixtures, in which some specific activation of oxygen was suspected; the balance of evidence failed to decide whether thermal or electrical factors predominated. Similar phenomena have more recently received a different explanation based on chain propagation (44). It must, however, be pointed out in this connection that unless electrical factors are fully under control, data based on limiting igniting pressures may be misleading, since the electrical characteristics of a gaseous mixture can be, and often are, fundamentally altered by the addition of a diluent gas.

The first experiments in which systematic control of electrical conditions was aimed at were made by Thornton (45-50, 63, 51-55), using the method of least igniting energy or current. His work included studies of many different types of igniting agent, and led to the fundamentally important observation that a given amount of electrical energy can possess vastly different igniting powers when dissipated in different forms. For example, a capacity spark was found to be considerably more effective in igniting certain gases than a spark produced by breaking a circuit containing inductance, and the incendivity of the latter type of discharge increased as the voltage applied to the circuit increased. From the undoubted specificity of the discharge characteristics which Thornton's work revealed, he concluded (46) that ionization was the effective cause of ignition. More recently, however, in the light of the results to be described later, which led to the excitation theory of ignition, Thornton has recognized that ionization is not the only factor to be considered (18).

#### THE THERMAL THEORY OF ELECTRICAL IGNITION

The question was reopened by Morgan (29). It had long been known that a spark discharge produced by an oscillation transformer, i.e., a coil or magneto, was a complex phenomenon consisting in the main of two

characteristically different parts. One such part is due to the discharge, on breakdown of the gap, of the energy stored in the distributed self-capacity of the secondary circuit, and is termed the "capacity component." The subsequent discharge of electromagnetic energy through the secondary circuit forms what is known as the "inductance component" of the discharge. Morgan found that if a magneto is shunted by a variable air condenser, the incendency of the spark so produced towards a particular gaseous mixture increased with increasing capacity. He concluded that the igniting power of an induction coil or magneto spark is associated chiefly with the capacity component, and only secondarily with the inductance component which follows it. Meanwhile Wheeler (59) had independently postulated that the necessary condition for ignition was that sufficient energy should be introduced to maintain for a sufficient time a sufficient volume of a gaseous mixture at or above its ignition temperature. Although experiments, designed to show whether incendency could be correlated with the thermal properties of the gaseous mixture concerned or with its speed of flame propagation, yielded negative results (59, 60), Wheeler found in the assumed general superiority of the capacity component in ignition a confirmation of a purely thermal view of electrical ignition phenomena, and jointly with Morgan and Taylor-Jones (43) put forward a thermal theory of ignition, ultimately depending on that assumption.

The theory was founded on analysis of the temperature distribution in a gas in the immediate neighborhood of various types of localized heat sources. Such analysis indicated that for a given amount of energy, an instantaneous point source was superior to a continued source and that a volume source was superior to a point source, and it was considered that these differences were sufficient to account for the marked effect which the precise mode of dissipation of a given amount of electrical energy had on its igniting power—as shown by the researches of Thornton and others—without reference to ionization or any other specific characteristic of the spark discharge.

The theory was put by Morgan in the form "the ignition of a gaseous mixture depends primarily . . . on the raising of a sufficient volume to a sufficient temperature (43)," with the corollary that "the heat energy required in the source to produce ignition is least when the heat is imparted instantaneously. When the rate of heat supply is less, a greater quantity of heat must be given to the gas before ignition can occur" (31). The theory was applied to various ignition phenomena (see Morgan (30, 31, 32, 34, 35), Morgan and Wheeler (36), Coward and Meiter (10), Taylor-Jones (42), and Holm (24)), nevertheless it embodied a principle which was inherently improbable. Taking the statement of the thermal theory

as set forth above, it is not difficult to show that it implies the view that the igniting power of a given quantity of energy lies dormant until the energy is converted into heat and thus increases with increasing lack of availability of such source energy. For temperature, a statistical measure of the mean kinetic energy of the random translational motions of the molecules of a system, is a fundamental conception which loses in significance as the entropy falls below the maximum consistent with the energy of the system. As in the case of a single molecule, the term "temperature" is meaningless when applied to mass motion. And since, according to the thermal theory, ignition calls for the raising of the gas to a sufficient temperature, it is clear that this view suggests that in the case of a source of least igniting energy the entropy/energy ratio of the system must be at a maximum before ignition can be determined therein. Coward and Meiter (10), as a result of their experiments, appear indeed to have arrived at this conclusion, because they state that "nothing in the results of (their) experiments suggests the intervention of any electrical effect of the spark . . . other than the normal effect of the degradation of its electrical energy."

#### CHARACTERISTICS OF GASEOUS COMBUSTION IN ELECTRIC DISCHARGES

About this time there came to light a set of facts relating to gaseous combustion in electric discharges which put the question of spark ignition in a new light, and enabled it to be divorced from the older standpoint of thermal ignition with which it had hitherto been linked. These facts will now be briefly reviewed.

A discharge between solid electrodes may take the form of either a low- or a high-tension arc, the essential difference being in the temperature of the cathode. The discharges employed in ignition are almost without exception of the high-tension type, and it has been shown by Finch and Cowen (14) that a high-tension arc dissipating energy at a surprisingly high rate can be maintained in an explosive gaseous mixture without causing ignition. In such a discharge, three luminous zones are ordinarily distinguishable: (i) the cathode and negative glows sheathing the cathode and constituting the cathode glow, (ii) the anode glow or spot, and, finally, (iii) the positive column between which and the cathode zone lies the Faraday dark space. The positive column can be wholly suppressed or varied in extent by a suitable choice of gap width, gas pressure, or current. Reduction of the positive column of a high-tension arc, maintained in an explosive mixture such as  $2\text{H}_2 + \text{O}_2$ , by decreasing the distance between the electrodes, in no way affects either the anode or the cathode glow, but proportionately reduces the rate of combustion (14). Therefore some combustion occurs in the positive column; once the positive column has been eliminated, a further reduction in gap width merely encroaches

on the Faraday dark space, but has no effect on the rate of combustion. It follows that combustion must be limited to the luminous zones of the discharge.

The rate of combustion in a discharge from which the positive column is absent is directly proportional to the current and independent of the nature of the anode material, but is profoundly affected by that of the cathode (14, 16). For example, dry  $2\text{CO} + \text{O}_2$  burns more than three times more rapidly at a silver cathode than at a copper cathode. It has been shown that this remarkable effect cannot be due to a difference in the cathode potential falls of different metals; it may therefore be concluded that in the absence of a positive column, combustion is confined to the cathode zone.

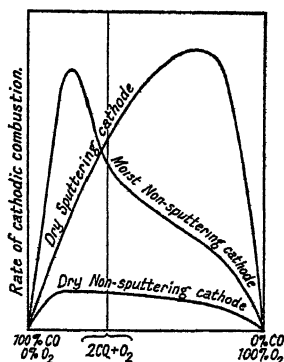


FIG. 1

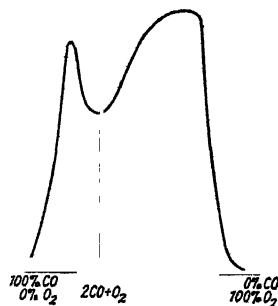


FIG. 2

FIG. 1. Showing the change in rate of cathodic combustion with composition in moist and dry carbon monoxide-oxygen mixtures at sputtering and non-sputtering cathodes.

FIG. 2. Showing the change in rate of cathodic combustion with composition in moist carbon monoxide-oxygen mixtures at a sputtering cathode.

In suitable conditions the cathode potential fall is independent of either the current or the gas pressure; thus the rate of combustion is directly related to the energy dissipated in the cathode zone. It has been established that the specific and very considerable influence which the nature of the cathode material exerts on the rate of cathodic combustion is not connected with the occurrence of heterogeneous combustion, as might at first sight be supposed, but that the effects are due to the influence of sputtered metal atoms, i.e., atoms of the cathode material torn from its surface and projected into the cathode zone under the influence of ionic bombardment.

Figures 1 to 4 summarize some of the results of a series of researches, for details of which reference must be made to the original papers (14, 15,

16, 19, 13). In these graphs the ordinates represent rates of cathodic combustion, expressed in terms of the ratio of the rate of combustion of the gas to the current carried by the discharge. Figures 1, 2, and 4 are drawn to the same scale.

Dry  $2\text{CO} + \text{O}_2$  burns slowly at a tantalum or tungsten, i.e., non-sputtering, cathode (figure 1), but at a freely sputtering cathode such as silver or gold, the metal atoms projected into the cathode zone effect an approximately fivefold increase in the rate of combustion, and a rather similar acceleration is brought about by the addition of water vapor (see figure 1) (16). The accelerating effects of steam and of metal atoms are not, however, additive, for the presence of moisture slightly reduces the rate of combustion of a  $2\text{CO} + \text{O}_2$  mixture at a sputtering cathode (19). Furthermore, the rôles played by steam and by metal atoms in overcoming the reluctance of carbon monoxide to burn cathodically must differ fundamentally, because steam is most active in promoting the combustion of mixtures rich in carbon monoxide, whereas the rate of combustion of carbon monoxide at a freely sputtering cathode attains a maximum when excess oxygen is present (figure 1) (19), whilst replacement of the excess of oxygen by helium or argon mainly results in a dilution effect. Finally, the independent modes of activity of steam and metal atoms in promoting the combustion of carbon monoxide-oxygen mixtures is established by the results recorded graphically in figure 2; when both steam and metal particles are present, the curve showing the relation between rate of cathodic combustion and mixture composition exhibits two characteristic maxima, one due to moisture when carbon monoxide is in excess, and the other due to sputtered metal atoms in oxygen-rich mixtures (19). Thus, steam and metal atoms do not interfere with each other to any material extent in promoting the cathodic combustion of carbon monoxide-oxygen mixtures.

From this and other cognate data it was concluded that the process of the combustion of carbon monoxide in different conditions may be represented as follows:

- (i) Dry carbon monoxide-oxygen mixtures in the absence of metal atoms:
  - (a)  $2\text{CO} = \text{CO}_2 + \text{C}$ , and
  - (b) C is burnt by oxygen.
- (ii) Dry carbon monoxide-oxygen mixtures in the presence of metal atoms:
  - (a)  $\text{Me} + \text{oxygen} = \text{MeO}$ , an unstable metal oxide, and
  - (b)  $\text{CO} + \text{MeO} = \text{CO}_2 + \text{Me}$
- (iii) Moist carbon monoxide-oxygen mixtures:
 
$$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$$

Carbon monoxide-oxygen-hydrogen mixtures containing not more than sufficient oxygen for complete combustion burn at either sputtering or

non-sputtering cathodes in such a manner that carbon dioxide is more rapidly formed than is steam (figure 3); thus the carbon monoxide appears to burn more rapidly than does the hydrogen. The rates of cathodic combustion occurring in such mixtures at non-sputtering cathodes have, however, little or nothing in common with those observed in the case of either moist or dry carbon monoxide-oxygen mixtures; carbon monoxide-oxygen-hydrogen mixtures burn in general not only much faster, but the manner in which the rate of combustion varies with increasing combustible

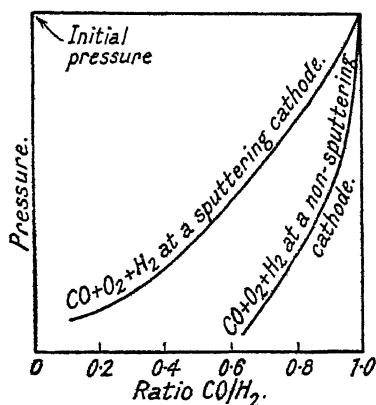


FIG. 3

FIG. 3. Preferential combustion of carbon monoxide in a carbon monoxide-oxygen-hydrogen mixture

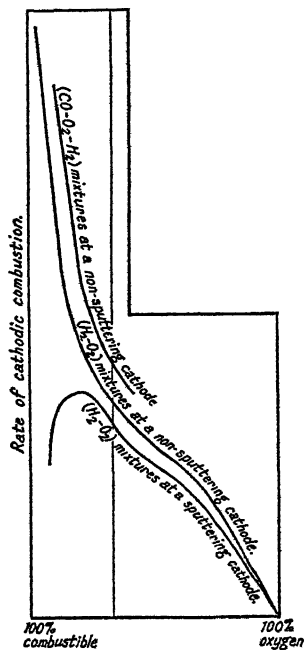


FIG. 4

FIG. 4. Cathodic combustion of hydrogen-oxygen and carbon monoxide-oxygen-hydrogen mixtures. Rate of combustion to same scale as in figures 1 and 2.

contents also bears no resemblance to that observed in the case of dry or moist carbon monoxide-oxygen mixtures (figure 1). A close parallel exists, however, between the rates of cathodic combustion of carbon monoxide-oxygen-hydrogen and hydrogen-oxygen mixtures; in both, the rates of combustion at a non-sputtering cathode increase rapidly and in a similar manner with increasing combustible contents (19, 17, 13) (figure 4). Furthermore, within the limits hitherto examined, a partial substitution of carbon monoxide by an equivalent amount of hydrogen has little or no



effect on the rate of combustion of carbon monoxide-oxygen-hydrogen mixtures. In view of these facts, it is difficult to resist the conclusion that, during the combustion of carbon monoxide-oxygen-hydrogen mixtures at a sputtering cathode, the hydrogen burns first and at a rate which in effect determines that of the mixture as a whole, and that the apparent preferential combustion, i.e., the more rapid disappearance of carbon monoxide, is due to oxidation by some product, or products, of the combustion of hydrogen which is thereby returned to the mixture; and, further, since the rate at which carbon monoxide burns when undergoing such preferential combustion is much higher than that observed in the case of dry carbon monoxide-oxygen mixtures, it follows that carbon monoxide is burnt far more readily by the product or products of the combustion of hydrogen than by oxygen.

Moreover, the extent to which carbon monoxide burns preferentially in carbon monoxide-oxygen-hydrogen mixtures is far greater when combustion proceeds at a sputtering cathode than otherwise (figure 3), although the total rate of combustion is greatly reduced, in some cases by as much as three times, by the presence of metal atoms (19). These facts strongly suggest (i) that carbon monoxide is burnt by at least two oxidation products of hydrogen, one of which is more highly oxygenated than the other, and thus, on reduction, leads to the return of less hydrogen to the burning mixture, and (ii) that metal atoms either prevent the formation of or decompose the oxygen-rich hydrogen combustion product, and in this manner not only increase the extent to which the carbon monoxide is burnt preferentially, but are also responsible for the reduction in the rate of combustion in carbon monoxide-oxygen-hydrogen mixtures observed at a sputtering cathode. This view is further supported by the fact that hydrogen-oxygen and carbon monoxide-oxygen-hydrogen mixtures containing combustible in sufficient excess all burn at a sputtering cathode at a practically similar rate, which is, within wide limits, independent of the composition of the mixture (19, 17).

In addition to steam, the chief oxidation products of hydrogen known to be formed within the cathode zone maintained in either steam or hydrogen-oxygen mixtures are hydroxyl, and possibly hydrogen peroxide, which has been detected, though only in small amounts, in the products issuing from the discharge (19, 17). Hydrogen, however, is present in profusion (22).

It is improbable for several reasons that hydrogen peroxide plays any material rôle, and the facts strongly suggest that it is OH which, like steam, is so active in burning carbon monoxide, and that metal atoms neither decompose OH, nor do they prevent its formation from steam, but that sputtered metal in some manner inhibits the formation of OH as

a direct intermediate product of the cathodic combustion of hydrogen to steam. Thus the combustion of carbon monoxide-oxygen-hydrogen mixtures at non-sputtering cathodes may be represented as follows:

- (a)  $\text{H}_2$  burns *via* OH to  $\text{H}_2\text{O}$ ,
- (b)  $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ , and
- (c)  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$

Oxygen-rich hydrogen-oxygen mixtures burn at relatively low rates at either a sputtering or a non-sputtering cathode. In the case of mixtures containing excess hydrogen, however, and burning at a non-sputtering cathode, combustion increases at a remarkable rate with increasing hydrogen concentration, an effect which is almost wholly suppressed by the presence of metal atoms (figure 4) (17). In the first place, these facts strongly suggest that both hydrogen and oxygen must be suitably excited before they can combine, and that the life of oxygen in the excited state is short, whilst that of the hydrogen is long. Further, the more than threefold reduction in the rate of cathodic combustion which can be and is effected by the presence of sputtered metal atoms can be reasonably explained, in accordance with the mechanism of the combustion of carbon monoxide-oxygen-hydrogen mixtures put forward above, as follows: Hydroxyl is an intermediate product in the normal combustion of hydrogen to steam. Metal atoms form with oxygen easily reduced oxides or unstable complexes which burn hydrogen to steam directly and thus suppress the intermediate formation of hydroxyl. Finally, since the rate of combustion of a hydrogen-rich hydrogen-oxygen mixture is much greater in the absence than otherwise of metal atoms, i.e., when OH is freely formed as an intermediate product, it may be concluded that OH in some manner powerfully promotes the combustion of hydrogen.

The fact that the rates of combustion of hydrogen-oxygen and of carbon monoxide-oxygen-hydrogen mixtures at a non-sputtering cathode increase rapidly and in a similar manner with increasing combustible contents (figure 4) suggests that the short life of oxygen in the suitably excited state for combustion with hydrogen is due to deactivation by collision with oxygen in some form or other, but not with hydrogen or carbon monoxide. Cool, arced, moist hydrogen contains much atomic hydrogen but reacts most reluctantly, if at all, with similarly arced oxygen, which is in a state of afterglow and rich in ozone undergoing decomposition (12); thus the respective levels of excitation to which hydrogen and oxygen must be raised are high if they are to combine directly and without the intervention of any promotor of combustion such as OH. It is well known, however, that steam dissociates to a measurable extent at comparatively low temperatures of the order of  $800^\circ\text{C}$ . It follows that the energy

required to bring about the decomposition of steam is far less than that necessary in order to excite hydrogen and oxygen sufficiently for them to combine directly. For thermochemical reasons, the most probable initial step in the mechanism of the decomposition of steam consists in the interaction of steam molecules, whereby hydroxyl and molecular hydrogen are formed. Herein lies a probable explanation of the striking fact, discovered by Smithells, Whitaker, and Holmes (40) that the ignitability of a  $2\text{CO} + \text{O}_2 + \text{H}_2$  mixture by a spark is greatly increased by a trace of steam. Thus, according to this view, a comparatively powerful discharge is required to ignite the rigidly dried mixture, because the initial formation of OH calls for the prior excitation of hydrogen and oxygen molecules to relatively high levels; in the case of the incompletely dried mixture, however, a much milder discharge suffices to produce hydroxyl by the decomposition of steam and thus to initiate combustion.

Concluding the summarized combustion mechanisms so far established: (i) hydrogen-oxygen mixtures in the absence of metal atoms: when the mixture is rigidly dried the initial step is (a)  $\text{H}_2 + \text{O}_2 = 2\text{OH}$ , but (b)  $2\text{H}_2\text{O} = 2\text{OH} + \text{H}_2$  when moisture is present; whereupon OH in some manner acts as a powerful promotor in the succeeding stages of combustion. (ii) Hydrogen-oxygen mixtures in the presence of metal atoms:  $\text{Me} + \text{oxygen} = \text{MeO}$ , and  $\text{H}_2 + \text{MeO} = \text{H}_2\text{O} + \text{Me}$ .

These results provided clear evidence that the cathode zone of a high-tension discharge is a region in which gas molecules are excited to states of specific excitation which determine their subsequent reactivity, and that the gas in the path of the discharge is not merely heated by passage of the current.

#### IGNITION BY HIGH-TENSION, DIRECT-CURRENT DISCHARGES

At a given gas pressure, a high-tension, direct-current discharge can be maintained in an explosive gaseous mixture up to a limiting current; above this current the mixture explodes. The transition from steady combustion to ignition was the subject of a separate investigation (14); in the case of  $2\text{H}_2 + \text{O}_2$  mixtures it was shown, *inter alia*, that: (i) Ignition occurs without lag immediately on attainment of a certain limiting current. (ii) A hyperbolic relationship exists between the gas pressure and the igniting current over a considerable range of conditions. (iii) A decrease in gap width, which results in a broadening out of the bright positive glow, increases the value of the igniting current.

On kinetic grounds, the concentration of ions, or of molecules or atoms excited to any particular state, is also approximately a hyperbolic function of gas pressure for conditions such as those under consideration, in which the potential drop across the discharge is constant. It follows, therefore,

that in the conditions of these experiments, ignition was determined by the attainment of a certain definite concentration of suitably excited molecules or atoms.

#### THE FUNCTION OF IONS

Ions, however, could not be excluded on the evidence so far available, although analyses of the rates of cathodic combustion of hydrogen and of carbon monoxide indicated that combustion was probably determined by excitation of the reactant molecules to states falling short of complete ionization. In the case of carbon monoxide a direct proof of this was furnished by a spectrographic examination (22). Spectrograms of the positive column and cathode zones of discharges at both sputtering and non-sputtering electrodes in carbon monoxide and in the mixture  $2\text{CO} + \text{O}_2$  revealed the presence of carbon monoxide bands, but no evidence of ionized carbon monoxide. Carbon monoxide molecules in the discharge were therefore excited, but not ionized; hence it was clear, at least in the case of carbon monoxide, that combustion was determined by excitation falling short of ionization.

#### EXCITATION THEORY OF ELECTRICAL IGNITION

From this and much other cognate evidence it became increasingly clear that the necessary prerequisite for the ignition of an explosive gaseous mixture was the setting up of a *sufficient concentration of suitably activated molecules*, and abundant indications existed that ignition by an electrical discharge depended on this specific activation and not on the fully degenerate activation associated with thermal energy, as postulated by the thermal theory of ignition. The two theories conflicted directly, and a crucial test between them was therefore devised (23). The experimental method employed is shown in figure 5.

Mixtures of carbon monoxide and air in their equivalent proportions were ignited by means of condensed discharges of known oscillation frequency, and the igniting powers of the sparks were determined in terms of minimum igniting pressures, conditions being so arranged that the effect of frequency on igniting power could be studied independently of (i) the total amount of energy dissipated or (ii) its rate of dissipation either during the first half-cycle or during the complete discharge.

The condenser was charged through a diode and discharged at a constant initial voltage of 8300 volts through a circuit containing a variable inductance but otherwise of negligible impedance. Hemispherical aluminum electrodes were used for the spark gap, this metal being chosen because of its low cathode potential fall and freedom from sputtering. A subsidiary spark gap discharging in a lagged chamber fitted with a thermo-

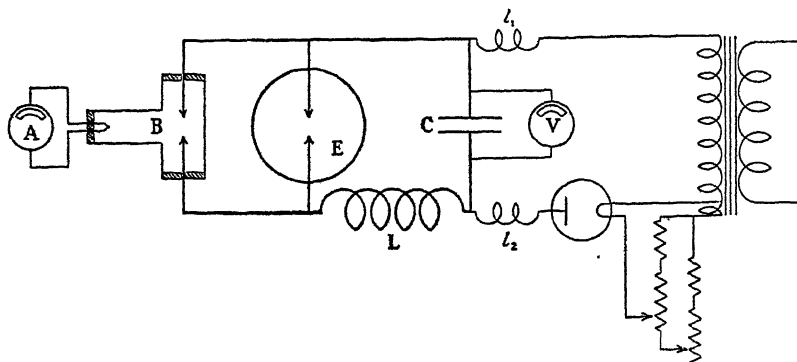


FIG. 5. Diagram of a condenser discharge circuit for ignition experiments (Finch and Thompson)

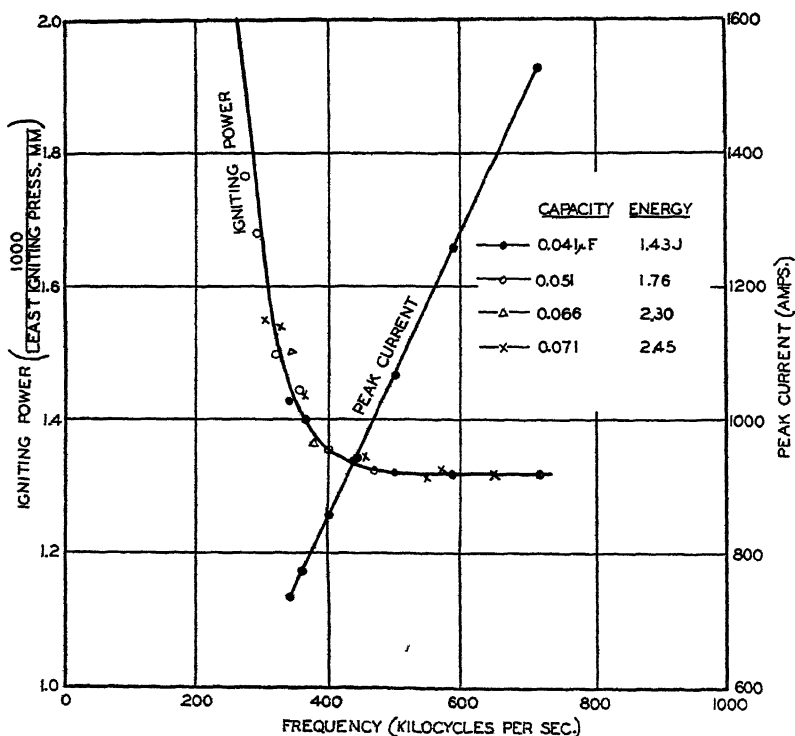


FIG. 6. Effect of frequency of discharge on its igniting power and on peak current. The peak current is for a capacity of  $0.041 \mu\text{F}$ ; other capacities gave similar curves.

couple furnished a means of comparing the relative energies of different sparks. Experiments were carried out over a range of frequencies for a number of different capacities. The results are summarized in figure 6.

It will be seen that for each value of the capacity the igniting power of the discharge increased with decreasing frequency, in spite of the fact that the energy dissipated by the discharge decreased with decreasing frequency. Furthermore, it will be observed that the frequency of the discharge exerted a considerably greater effect on its igniting power than did its total energy. It is not difficult to see also that the igniting power of the spark was not determined by the value of the peak current. The experiments showed that the igniting power of a spark due to the discharge of a condenser through an inductive circuit is determined by the natural frequency of the circuit to such an extent that a suitable decrease in frequency may completely outweigh the effect of any possible reduction in igniting power due to either a decreased amount or rate of energy dissipation, or both, by either the first half-oscillation of a spark or by the entire discharge. According to the thermal theory, however, "ignition depends on the heating of a sufficient volume of the gas by conduction to a sufficient temperature" (34), which also implies that "the heat energy required in the source to produce ignition is least when the heat is imparted instantaneously. When the rate of heat supply is less, a greater quantity of heat must be given to the gas before ignition can occur" (31). Hence it is clear that the conflict between the thermal theory and the facts set forth herein is complete. The mechanism of electric spark ignition, therefore, and indeed of ignition as a whole, cannot be adequately explained in terms of any purely thermal theory. On the other hand, the excitation hypothesis is consistent with, and capable of, explaining these facts. For, according to this view, ignition being primarily determined by the setting up of a sufficient concentration of suitably activated molecules, the imparting of energy to the molecules in such a manner as to bring about either an insufficient or excessive degree of activation is wasteful from the point of view of causing ignition. Now it is well known that the greater the frequency of a condensed discharge, the higher is the level to which the molecules are thereby activated. Thus the high-frequency spark is in general a rich source of ionization, whereas the low-frequency arc spectrum reveals mainly the presence of neutral atoms or molecules, and it may be concluded that in the present case a reduction in frequency resulted in an increase in the ratio between energy usefully expended in the production of suitably activated molecules and that otherwise dissipated.

#### IGNITION BY THE COIL DISCHARGE

There remained for solution the problem of the mechanism of ignition by a coil discharge, which is the case of practical importance. A systematic study of the phenomenon called for an investigation of the respective rôles played by the two components of the coil discharge, and it was desirable to be able to modify or suppress one without materially affecting

the other. Means of achieving this emerged from a consideration of the theory of the ignition coil based on a cathode-ray oscillographic study of the discharge.

#### CHARACTERISTICS OF THE IGNITION COIL DISCHARGE

Neglecting the secondary resistance, the general coil circuit equations may be written:

$$L_1 di_1/dt + L_{12} di_2/dt + R_1 i_1 + e_1 = 0$$

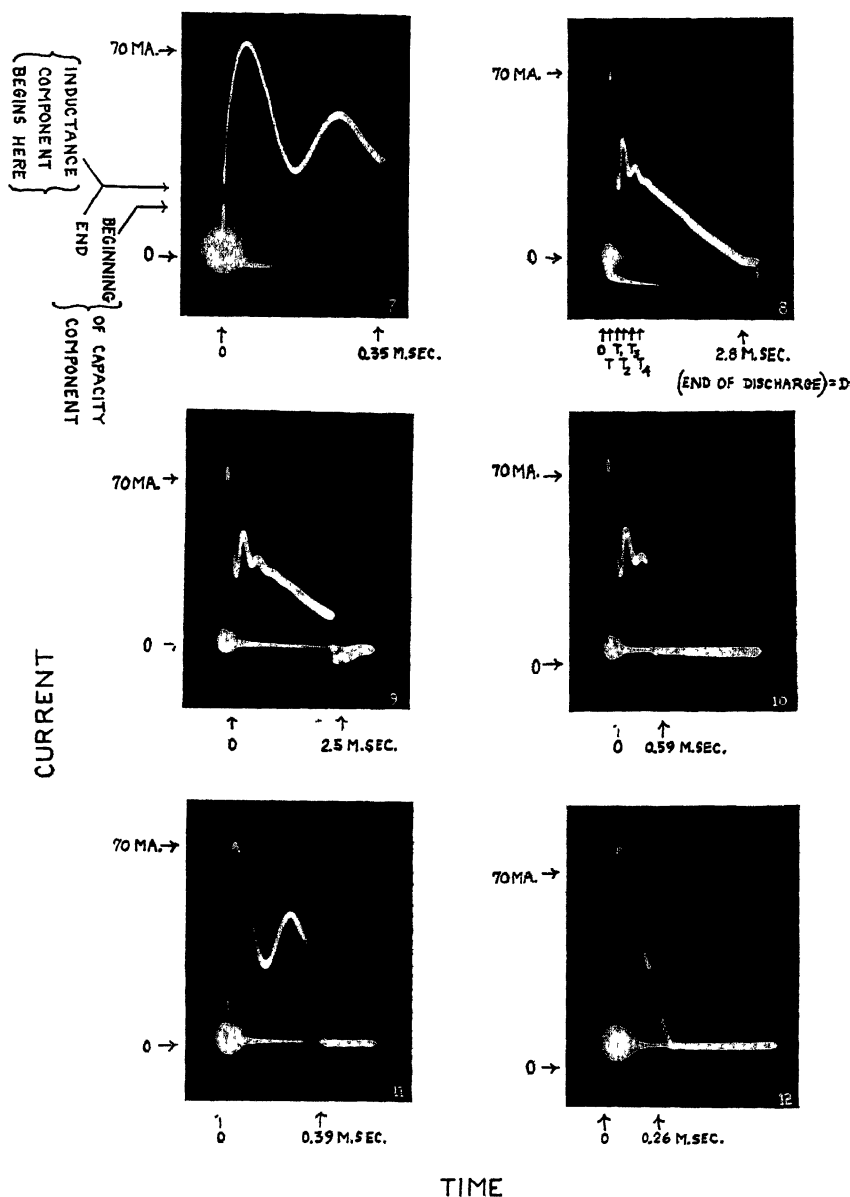
and

$$L_2 di_2/dt + L_{21} di_1/dt + e_2 = 0$$

where  $L_1$ ,  $L_2$  and  $C_1$ ,  $C_2$  are the primary and secondary inductances and capacities respectively,  $R_1$  is the primary resistance,  $i_1$  and  $i_2$  are the primary and secondary currents,  $e_1$  and  $e_2$  are the potential differences across the condensers,  $L_{12}$  and  $L_{21}$  are the coefficients of mutual induction of the secondary on the primary and of the primary on the secondary, respectively, and  $t$  is the time. Taylor-Jones (41) has solved these equations for two special cases, i.e., (i) open-circuited secondary and (ii) secondary closed by an ohmic resistance, neither of which, however, is of much interest from the point of view of ignition, because, in the normal circumstances of its use, the coil is required to furnish a spark across a short fixed gap, the breakdown potential of which is much smaller than the maximum voltage which the coil is capable of exerting. The above equations can, however, be solved for the case of practical interest, provided the voltage-current characteristic of the spark be known.

Cathode-ray oscillographic analysis (20, 5) of a typical ignition coil discharge led to the following results. Upon breaking the primary circuit the discharge voltage rises in a manner determined by the coil constants and spark gap conductance to the breakdown potential of the gap, and then falls with extreme rapidity to a value at which it remains sensibly constant throughout the remaining life of the discharge. The corresponding current-time trace is shown completely in figure 8: the initial part of the current-time trace is best understood from figure 7, which was taken with a suitable air-dielectric capacity shunting the spark-gap. The gap in the trace near the origin corresponds to the discharge of the capacity component; the trace is invisible here because both the frequency and the amplitude of the discharge are exceedingly high. For a certain ignition coil assembly, for example, the frequency was of the order of  $10^7$  cps, and the peak value of the current was calculated to be about 30 amp.

The spark potential is virtually constant and independent of the current during the life of the discharge; therefore no current flows in the secondary self-capacity during the discharge, and  $L_{12} = L_{21}$ . Hence it may be shown



FIGS. 7-12. Oscillograph records of induction coil spark discharges. FIG. 7, taken with a suitable air-dielectric capacity shunting the spark gap; FIG. 8, complete discharge; FIG. 9, late cut-off of discharge; FIG. 10, cut-off at  $T_3$ ; FIG. 11, cut-off at  $T_2$ ; FIG. 12, cut-off at  $T_1$ .



that in normal sparking conditions the inductance component rises to a maximum value of  $2i_0e^{-a\pi/2\omega}$  and executes damped oscillations of initial amplitude  $ni_0$  about a linear axis, the slope of which is given by  $-e_2/L_2$ . The total duration of the discharge is given by  $Mi_0/e_2$ , where  $M = L_{12} = L_{21}$ .

#### CONTROL OF SPARK COMPONENTS

Thus the difference between the capacity and inductance components of the discharge is clear and fundamental; their separation and control was carried out as follows: *The capacity component* can be practically eliminated by including in the secondary circuit a suitable diode run under such conditions as virtually to arrest the high currents of the capacity component whilst passing the inductance component unimpaired (5). In this manner the value of the capacity component may be reduced to the negligible quantity represented by the charging up of the gap inter-electrode capacity to the breakdown potential. *The inductance component*: Since the primary and secondary circuits in an ignition coil are closely coupled, the effective primary inductance must be small as long as the secondary is short-circuited by a spark. Hence if the primary circuit is closed during the life of the discharge, the primary current should build up exceedingly rapidly and since the energy would otherwise for the most part have appeared in the discharge, the latter would be expected to terminate abruptly. Analysis by means of the theory outlined above indicated that the spark should, in fact, terminate exceedingly abruptly, and a double interrupter (11) was designed which enabled the primary circuit to be remade at short and controllable intervals after break. The effect on the inductance component can be seen in the oscillograms (figures 7 to 12). Variation of the break-remake period, controlled by oscillographic observation, enabled the life of the inductance component to be varied from practically zero to its full value. The amplitude and frequency of the inductance component were controllable through the primary current and capacity.

#### COIL IGNITION OF STAGNANT GASES

A series of critical experiments was planned to find whether the statement of Morgan and others (*loc. cit.*) that coil ignition is effected by the capacity and not by the inductance component is a justifiable generalization. The discharges employed were normal in every respect except that the life of the inductance component was varied as shown in figures 7 to 12. Table 1 shows a typical series of results with the explosive mixture  $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$  (4). It was immediately clear that the igniting power of the spark decreased with progressive suppression of the inductance component, and when the least possible amount of inductance component

energy was allowed to pass, the mixture failed to ignite at the highest pressure which could be employed without danger of shattering the explosion vessel. It may be emphasized that the capacity component was not reduced by progressive suppression of the inductance component, but must have increased for the igniting sparks; Paschen's law is known to hold with accuracy over the range of pressures employed, and the breakdown potential of the gap, and hence the energy of the capacity component, must therefore have increased with increasing gas pressure.

The same principle was shown to apply to ignition of the mixtures  $2\text{H}_2 + \text{O}_2$  and  $\text{CH}_4 + \text{O}_2$ , but with the latter, cut-off of the inductance component had considerably less effect on the igniting power of the discharge. Thus, whilst a  $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$  mixture was relatively insensi-

TABLE 1  
*Relation of coil ignition to inductance component*

CUT-OFF (SEE FIGURES 8 TO 12)	INDUCTANCE COMPONENT ENERGY	DURATION OF INDUCTANCE COMPONENT	IGNITING POWER = 1000/LEAST IGNITING PRESSURE	LEAST IGNITING PRESSURE
	<i>m.J.</i>	<i>m.sec.</i>	<i>mm.</i>	<i>mm.</i>
End of discharge.....	20.5	2.81	9.43	106
T <sub>4</sub> .....	9.2	0.79	7.70	130
T <sub>3</sub> .....	7.4	0.59	7.41	149
T <sub>2</sub> .....	5.2	0.39	6.50	154
T <sub>1</sub> .....	2.4	0.20	5.13	195
T.....	ca. 0.15	0.02	4.26	235

tive to ignition by the capacity component as compared with  $\text{CH}_4 + 2\text{O}_2$ , the position was reversed when the energy associated with the inductance component was increased to more than 10% of its maximum possible value.

It was clear therefore that the interaction of the spark and combustible gas molecules was complex and specific, and a study of the effects of further separation of the induction coil variables was necessary. As a final step, therefore, an investigation was made of the igniting powers of spark discharges modified in such ways as were necessary to isolate, not only the effect of the capacity component, but also the effects of the peak currents and duration of the inductance component (5). The discharge circuit conditions employed are shown in table 2.

With a normal inductance component duration the results were as shown in table 3.

Comparing the results for circuit conditions B and C(a) in the mixture  $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$  it will be seen that elimination of the capacity component of the discharge had an exceedingly small effect on its igniting

TABLE 2  
*Discharge circuit conditions employed*

CIRCUIT CONDITIONS	NATURE OF DISCHARGE	CURRENT-TIME OSCILLOGRAM
A. Unmodified . . . . .	Normal coil discharge	Figure 8
B. Diode in series with gap shunted by condenser and filament fully heated . . . . .	Normal coil discharge	As in A
C. Diode without shunting condenser: (a) filament fully heated . . .	Negligible capacity component; inductance component unimpaired	Figure 14
(b) filament underrun . . . . .	Negligible capacity component; normal (or nearly so) inductance component duration, but oscillations more or less damped out, according to extent of under-running	Figures 15 to 19
D. Diode shunted by condenser; filament cold . . . . .	Normal capacity component; negligible inductance component	
E. Diode as in D but without condenser . . . . .		

TABLE 3  
*Results with a normal inductance component duration*

CIRCUIT CONDITIONS	LEAST IGNITING PRESSURE	IGNITING POWER	CAPACITY COMPONENT ENERGY	INDUCTANCE COMPONENT	
				Energy	Duration
Mixture $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$					
	<i>mm.</i>		<i>m.J.</i>	<i>m.J.</i>	<i>m.sec.</i>
A	92.5	10.8	0.62	29.8	3.66
B	108.0	9.3	0.84		
C(a)	111.0	9.0	0.89		
D	No ignition at 304.0	3.3	6.7		
E	No ignition at 313.0	3.2	7.1		
Mixture $\text{CH}_4 + \text{O}_2$					
A	89.5	11.2	0.58	23.8	2.67
B	90.5	11.1	0.59		
C(a)	92.0	10.8	0.61		
D	224	4.5	3.6		
E	No ignition at 250	4.0	4.5		

power, and the mixture  $\text{CH}_4 + \text{O}_2$  gave a similar result. The capacity component alone (circuit condition D) failed to ignite a  $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$  mixture at the highest pressure which could be safely employed; in  $\text{CH}_4 + \text{O}_2$  ignition could be brought about by its sole agency, but at a greatly increased pressure.

The effect was even more striking when the inductance component energy was reduced by cutting off to a value nearer the capacity component

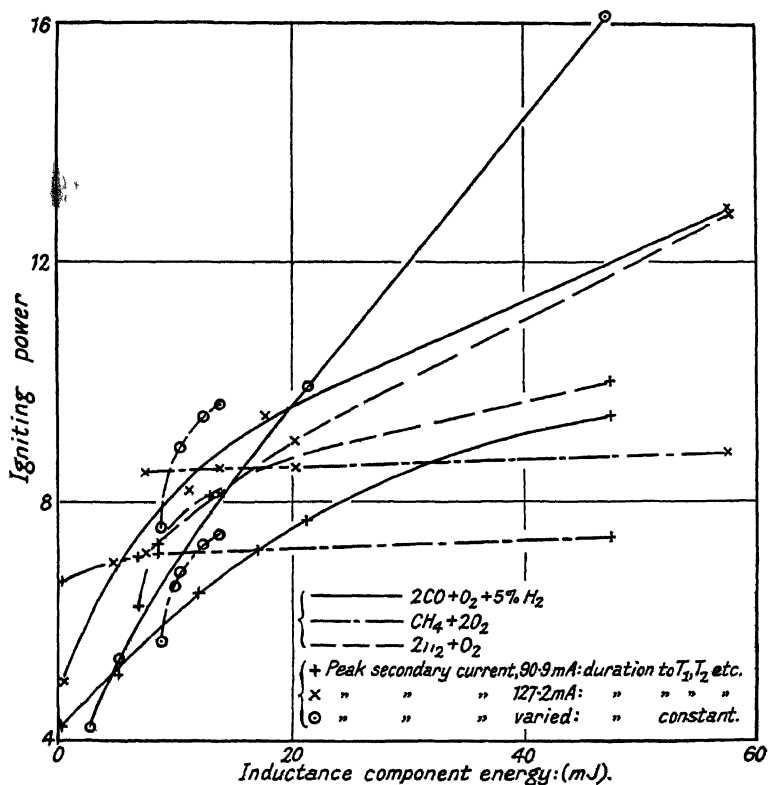
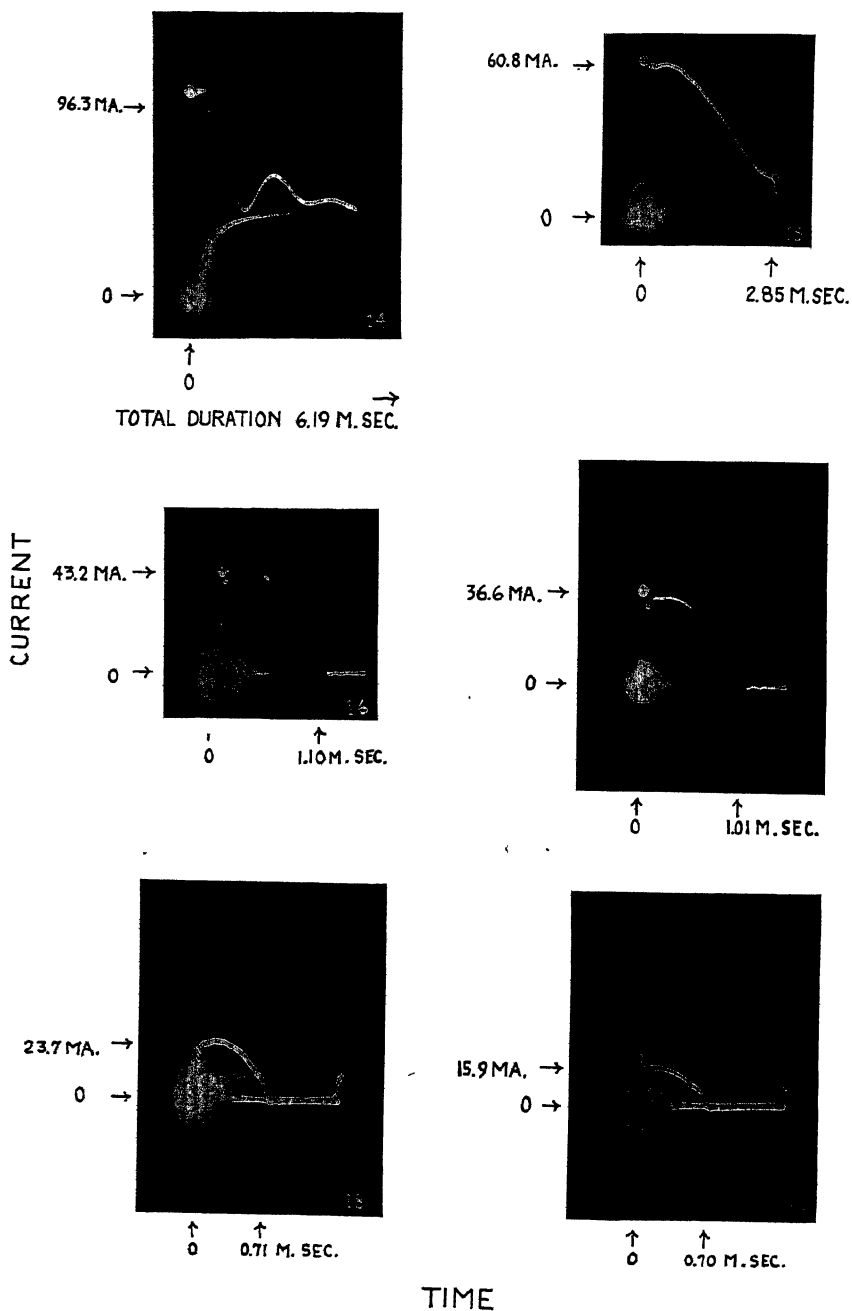


FIG. 13. Relation of igniting power of spark discharges to the energy in the inductance component for various gas mixtures.

energy. For example, with an inductance component duration of 0.38 m.sec. (i.e., a duration nearly half that shown in figure 19) inductance component energy (without associated capacity component) amounting to 5.11 mJ. ignited a  $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$  mixture at 152 mm., while capacity component energy of 8.8 mJ., without any succeeding inductance component energy, failed to ignite at a pressure of 350 mm.; the behavior



FIGS. 14-19. Oscillograph records of induction coil spark discharges

of methane was similar. These results not only bring out the relative inefficiency of a high-frequency oscillatory discharge as a source of ignition, but also enable the conclusion to be drawn that the igniting power of any subsequent inductance component is but little, if at all, enhanced by a preceding capacity component of dimensions similar to that met with in normal coil practice.

Variation of the inductance component energy, the peak current, and discharge life gave results which are summarized in figure 13. These again show clearly that the igniting power of the coil discharge is associated in the main with its inductance component, and, further, that not only the total energy of this component but also the peak and mean rates of dissipation of such energy influence the igniting power to extents which vary with the nature of the explosive mixture. For example, whilst in the case of all the mixtures an increase in either the peak rate of dissipation of energy or the total amount of energy resulted in an increase of igniting power, the influence of the total duration of the discharge varied according to the nature of the gas mixture. Thus, prolongation of the discharge beyond the second inductance component oscillation failed to effect any pronounced increase in the igniting power in the case of the methane mixture, whereas with  $2\text{H}_2 + \text{O}_2$ , and even more so in the case of  $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$ , the igniting power of the discharge increased steadily with increasing duration. With a damped and partially cut-off inductance component (as in figures 15 to 19) dissipating, e.g., 10 mJ., the order of decreasing sensitivity to ignition of the mixtures was  $2\text{H}_2 + \text{O}_2$ ,  $2\text{CO} + \text{O}_2 + 5\%\text{H}_2$ ,  $\text{CH}_4 + \text{O}_2$ ; on the other hand, dissipation of a similar amount of energy in the form of a normal undamped, but suitably cut-off inductance component (as in figures 7 to 12) resulted in an inversion of this order (see figure 13), thus confirming the fact already brought out that whilst methane was more particularly sensitive to the peak rate of energy dissipation, the ignition of the other mixtures could be brought about more efficiently by increasing the life of the discharge at the expense of the peak rate of energy dissipation, the total spark energy remaining otherwise unchanged.

#### SPARK IGNITION IN THE INTERNAL-COMBUSTION ENGINE

In the case of the experiments so far discussed, the ignition pressures were of the order of 0.1 to 0.2 atm., and the gas was both cool and stagnant. In the engine, however, the gas pressure at the moment of ignition is of the order of 10 atm., the gas is hot as a result of preheating and adiabatic compression, and is furthermore in a highly turbulent state. In order to bring out the practical bearing of the results obtained with stagnant gases, further experiments in which account was taken of these important changes

in conditions were carried out with a standard four-cylinder petrol engine (18). For details, the original paper must be consulted; among the more important points established were the following: (i) Power output, efficiency, and speed were alike unaffected by cutting off the latter part of the inductance component, so that the total spark duration was reduced, in one case, for example, from 2.0 to 0.5 m.sec. (ii) Variation of peak secondary current in the inductance component was also without effect on the engine characteristics. (iii) When the duration of the discharge was reduced sufficiently, misfiring occurred, and it was proved that the misfires were due to the occasional failure of the spark to jump the plug points, and not to the failure of the spark to ignite the explosive mixture. In the engine cylinder the conditions are so far removed from the limits that the igniting power of any spark furnished by the coil is greater than the least igniting value, and even if the spark consists only of the capacity component of the discharge, ignition occurs without fail.

The results proved that the only part of the ignition coil discharge required for ignition of the explosive mixture in an internal-combustion engine is the capacity component, the discharge of which can be insured in spite of a relatively high plug conductance by the retention of only a short initial portion of the inductance component, and the discharge duration can be reduced to one-tenth and possibly much less, without affecting either the igniting properties of the spark or the performance of the engine.

#### CONCLUSION

The researches which have been outlined above enable the view that electrical ignition is attributable to purely thermal effects of the spark to be dismissed. For not only has a large body of evidence been accumulated which shows that an electrical discharge is a region in which gas molecules are activated directly to states in which they are capable of taking part in the process of combustion, but it has also been shown experimentally that electrical ignition does not possess the characteristics which a purely thermal process of ignition would require. The facts relating to the ignition of gases, so far as they are now known, are, however, consistent with the view that combination is determined by a prior excitation of the molecules to suitable energy levels; excitation falling short of, or exceeding, such levels leads in the main to waste of igniting energy. According to this quite general "excitation" view of ignition, temperature, as a measure of collision frequency, is only of secondary significance. Heat is but one of several forms of energy capable of giving rise to suitable excitation and, owing to the random element, by no means necessarily the most efficient.

The further definition of the precise mechanism by which an electrical

discharge initiates an explosion in any particular gaseous mixture must depend on a full exploration of that system. Sufficient has been outlined above to show that the combustible gases which have so far been examined, i.e., carbon monoxide, hydrogen, and methane, differ characteristically in their response to discharges of various types. No attempt will be made here to explain the possible causes of the specific influence of the combustible gas; work shortly to be published on the cathodic combustion of methane bears on this point. As an indication of the lines along which many of the phenomena of ignition may be quantitatively expressed in terms of the rates at which activation and deactivation occur in various types of discharge, a paper by Mole (25) may be consulted.

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## THE IGNITION OF GASES BY LOCAL SOURCES

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Although the ignition of gases by local sources (mainly electric sparks) has been the subject of extended experimental investigations, there has been very little theoretical consideration of this topic. A paper by Taylor-Jones, Morgan, and Wheeler (7), one by Silver (6), and another by Mole (2) exhaust the list. At present the literature on ignition seems to consist mainly of an enormous collection of experimental data with insufficient theoretical basis to coördinate the data, to indicate the significance of experimental results, or to supply a ground for prediction. It was therefore felt that a theoretical study, even if only partially correct, might indicate lines of research that would help to eliminate the somewhat confused state of the literature on the subject.

### PHYSICAL ASSUMPTIONS

In order to treat the problem mathematically, it is necessary to adopt a definite physical mechanism for the process. We conceive of the problem of the ignition of gases as follows: In a combustible gaseous mixture contained in a large vessel there is an arrangement for rapidly releasing energy within a small volume at a distance from the walls, for example, by passing an electric spark. It is assumed that the energy instantaneously heats up a small spherical volume and also creates active particles. These active particles are the chain carriers of the chain-reaction theory; it is not necessary to state whether they are ions, atoms, molecules with an excess of energy, or something else. It is also not necessary to specify the mechanism by which these active particles are created, but simply to assume that the release of energy does create them. The following processes then take place: There is a heat-generating reaction which is assumed to proceed at a rate proportional to the concentration of active particles, but this concentration varies with distance and time because the active particles are diffusing through the gas, and in addition are increasing in number at a rate proportional to their concentration; that is, chain branching is occurring. We are interested mainly in temperature, and so the chemical reaction enters the picture only insofar as it generates

heat; it is not necessary to make any statements about the mechanism of the reaction except that it proceeds at a rate proportional to the concentration of active particles. Similarly, no particular mechanism for chain branching need be introduced.

Now the temperature at the center of the sphere tends to fall because of conduction of heat away from it, and to rise because of the heat generated. In some cases it rises continuously, and in others it shows a drop after a time (figure 1). Some criterion for ignition is needed, and the most natural one to use is the requirement that the temperature at the

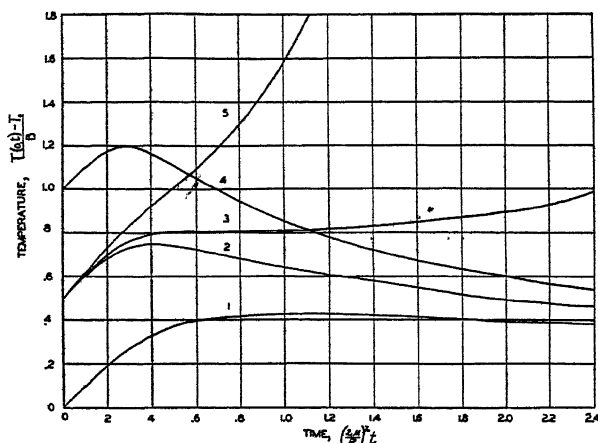


FIG. 1. Temperature at the origin for various values of  $A$  and  $m$

	$A$	$m$	
Curve 1.	0	0	No ignition
Curve 2.	0.5	0	No ignition
Curve 3.	0.5	0.64	Ignition, at limit
Curve 4.	1	0	No ignition
Curve 5.	0.5	1	Ignition

$$B = \frac{Qn_0R^2}{4k}$$

center of the sphere shall never fall. This can be justified by the fact that both the rate of the heat-generating reaction and of chain branching increase with increasing temperature, so that a temperature drop would slow them down, thus causing a further drop in temperature, and eventually making the reaction stop altogether.

In the following section the partial differential equations for the concentration of active particles and for temperature are stated and solved. Then the criterion for ignition is applied, giving a relation between the physical constants which must hold for ignition to take place.

It is assumed that the diffusion coefficient of the active particles is equal to the thermometric conductivity (thermal conductivity divided by specific heat per unit volume) of the gas through which they diffuse. If the active particles and the gas are the same molecular species, this is the result given by the elementary kinetic theory of gases (1). This is not quite exact, but the difference is not serious; experimental values for the ratio of diffusion coefficient to thermometric conductivity lie between 0.7 and 1. It is not impossible to solve the equations without this assumption, but the result is not enough closer to physical reality to justify the greatly increased complications.

It is obvious that many factors have been omitted from the picture given above. The rates of the heat-generating reaction and of chain branching are not merely proportional to the concentration of active particles, but are also functions of temperature. The effects of changes in pressure and of the presence of burned gas have also been left out of consideration. However, an attempt is not being made to set up a mechanism for the complete course of the reaction. This discussion is concerned only with a condition for ignition, and since the question as to whether ignition takes place or not is decided within a very short time, it is reasonable to assume that these omitted factors do not change very greatly within this time.

#### SOLUTION OF EQUATIONS

To make clear exactly what is involved, we restate in more general terms the problem which is treated here.

Consider a heat-conducting medium of infinite extent which is initially at temperature,  $T_0$ , except within a sphere of radius,  $R$ , where the initial temperature is  $T_1$ . At the start this sphere is filled with active particles in the concentration  $n_0$  per unit volume. These active particles diffuse through the medium; each generates  $Q$  units of heat in unit time and they increase in number at a rate proportional to their concentration. We wish to determine the relation that must exist among the physical constants for the temperature at the center of the sphere never to decrease.

The differential equation for the concentration of active particles is

$$\frac{\partial n}{\partial t} = \mu^2 \nabla^2 n + \alpha n \quad (1)$$

with the initial condition

$$\left. \begin{array}{l} n = n_0 \text{ for } 0 \leq r < R \\ n = 0 \text{ for } r > R \end{array} \right\} \text{ when } t = 0 \quad (2)$$

where  $n = n(r, t)$  is the concentration of active particles at a distance  $r$  and time  $t$ ,

$\mu^2$  = diffusion coefficient,

$\nabla^2$  = Laplacian differential operator, here  $\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)$

$\alpha$  = branching coefficient, and

$n_0$  = initial concentration in the sphere of radius  $R$ .

Equation 1 is merely the diffusion equation (4) with the additional term  $\alpha n$  giving the rate of increase of active particles.

To solve this put  $n = e^{\alpha t} f(r, t)$ . Then  $f(r, t)$  satisfies the diffusion equation (that is, equation 1 without the branching term  $\alpha n$ ) and the same initial condition. This has the solution (5)

$$f(r, t) = n_0 U(r, t)$$

where

$$U(r, t) = \frac{1}{2} \left[ \operatorname{erf} \left( \frac{R+r}{2\mu\sqrt{t}} \right) + \operatorname{erf} \left( \frac{R-r}{2\mu\sqrt{t}} \right) \right] + \frac{\mu}{r} \sqrt{\frac{t}{\pi}} \left[ e^{-\left( \frac{R+r}{2\mu\sqrt{t}} \right)^2} - e^{-\left( \frac{R-r}{2\mu\sqrt{t}} \right)^2} \right] \quad (3)$$

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-s^2} ds \quad (4)$$

being the error function or probability integral. Then

$$n(r, t) = n_0 e^{\alpha t} U(r, t) \quad (5)$$

is the solution of equations 1 and 2.

Since the function  $U(r, t)$  is to be used again, it is worth noting its meaning. As here introduced,  $U(r, t)$  gives the concentration of diffusing particles in an infinite medium when the initial concentration is 1 within a sphere of radius  $R$ , and 0 outside this sphere. Since the heat conduction equation (3) is of the same form as the diffusion equation,  $U(r, t)$  also gives the temperature in an infinite medium due to an initial temperature of 1 within the sphere and of 0 outside.

$U(r, t)$  can also be regarded in a slightly different manner. Instead of considering an initial temperature distribution, consider an instantaneous spherical volume source of heat which generates enough heat to raise the temperature of the sphere from 0 to 1. If this generation of heat occurs at time  $t = 0$ , the temperature will be given by  $U(r, t)$ . If it occurs at time  $t = \tau$ , the temperature at any later time will be given by  $U(r, t - \tau)$ .

These considerations will be used in finding the temperature distribution in the gas.

The partial differential equation for temperature is

$$\frac{\partial T}{\partial t} = \mu^2 \nabla^2 T + \frac{Q}{c} n(r, t) \quad (6)$$

with initial condition

$$\left. \begin{aligned} T &= T_1 \text{ for } 0 \leq r < R \\ T &= T_0 \text{ for } r > R \end{aligned} \right\} \quad \text{when } t = 0 \quad (7)$$

where  $T = T(r, t)$  is the temperature at distance  $r$  and time  $t$ ,

$\mu^2$  = thermometric conductivity (The same symbol is used as for diffusion coefficient because these are assumed equal as explained above.),

$Q$  = quantity of heat generated in unit time by the action of each active particle,

$c$  = specific heat of unit volume,

$T_1$  = initial temperature of the sphere of radius  $R$ , and

$T_0$  = initial temperature outside this sphere.

Equation 6 is the heat conduction equation (3) with the additional term  $\frac{Q}{c} n(r, t)$ , which gives the rate of temperature rise due to the heat produced by the action of the active particles.

This may be solved as follows. Put

$$T = T_0 + (T_1 - T_0) U(r, t) + V(r, t) \quad (8)$$

Then  $T_0 + (T_1 - T_0) U(r, t)$  satisfies the heat conduction equation (that is, equation 6 without the term  $\frac{Q}{c} n$ ) and the initial condition.  $V(r, t)$  must then satisfy equation 6 and vanish everywhere when  $t = 0$ ; it is the temperature due to a heat source generating  $Qn(r, t)$  units of heat in unit time.

Now, as noted before, the temperature due to an initial distribution can be reinterpreted as that due to an instantaneous heat source. The temperature due to a spherically symmetric initial distribution,  $\phi(r)$ , is (5)

$$\frac{1}{2\mu r \sqrt{\pi t}} \int_0^\infty \phi(\rho) e^{-\left(\frac{r-\rho}{2\mu\sqrt{t}}\right)^2} \rho d\rho \quad \text{(with } \phi(-\rho) \text{ put equal to } \phi(\rho))$$

---

\*  $U(r, t)$  is, of course, obtained by putting

$\phi(\rho) = 1$  for  $-1 < \rho < 1$

$\phi(\rho) = 0$  elsewhere

Then the temperature due to an instantaneous volume source which generates  $Qn(r, t)$  units of heat at time  $t = \tau$  is

$$W(r, t; \tau) = \frac{1}{2\mu r \sqrt{\pi(t-\tau)}} \int_{-\infty}^{\infty} \frac{Q}{c} n(\rho, \tau) e^{-\left(\frac{\rho-r}{2\mu\sqrt{t-\tau}}\right)^2} \rho \, d\rho \quad (9)$$

Since  $W(r, t; \tau)$  is the temperature at  $r$  and  $t$  due to a source at time  $\tau$ , the temperature due to the continuous source  $Qn(r, t)$  can be obtained by integrating  $W(r, t; \tau)$  for  $\tau = 0$  to  $\tau = t$ . Thus,

$$V(r, t) = \int_0^t W(r, t; \tau) \, d\tau \quad (10)$$

The reasoning by which this result has been obtained has been more physical than mathematical. A more rigorous proof of the fact that  $V(r, t)$  satisfies equation 6 can be given along the following lines. First note that  $W(r, t; \tau)$  satisfies

$$\frac{\partial W}{\partial t} = \mu^2 \nabla^2 W \quad (11)$$

for all  $\tau < t$ , as can be shown by direct calculation. Then

$$\frac{\partial V}{\partial t} = \int_0^t \frac{\partial W}{\partial t} \, d\tau + \lim_{\tau \rightarrow t} W(r, t; \tau) \quad (12)$$

It can be shown that

$$\lim_{\tau \rightarrow t} W(r, t; \tau) = \frac{Q}{c} n(r, t) \quad (13)$$

as follows: Put  $\rho = r + 2\mu\sqrt{t-\tau}\lambda$  and substitute in equation 9; then

$$\begin{aligned} W(r, t; \tau) &= \frac{1}{r\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{Q}{c} n(r + 2\mu\sqrt{t-\tau}\lambda, \tau) e^{-\lambda^2} (r + 2\mu\sqrt{t-\tau}\lambda) \, d\lambda \\ &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{Q}{c} n(r + 2\mu\sqrt{t-\tau}\lambda, \tau) e^{-\lambda^2} \, d\lambda \\ &\quad + \frac{2\mu\sqrt{t-\tau}}{r\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{Q}{c} n(r + 2\mu\sqrt{t-\tau}\lambda, \tau) \cdot e^{-\lambda^2} \lambda \, d\lambda \end{aligned}$$

Putting  $\tau = t$ , the second integral vanishes and the first is

$$\frac{Qn(r, t)}{c} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\lambda^2} \, d\lambda = \frac{Qn(r, t)}{c}$$

giving equation 13. Then,

$$\mu^2 \nabla^2 V(r, t) = \mu^2 \int_0^t \nabla^2 W(r, t; \tau) \, d\tau = \mu^2 \int_0^t \frac{\partial W}{\partial t} \, d\tau \quad (14)$$

from equation 11.

From equations 12, 13, and 14 it follows that

$$\frac{\partial V}{\partial t} = \mu^2 \nabla^2 V + \frac{Q}{c} n(r, t)$$

showing that  $V(r, t)$  satisfies equation 6.

Substituting the value of  $n(r, t)$  from equation 5 in equation 9 and carrying out the integration<sup>1</sup> there results

$$W(r, t; \tau) = \frac{Qn_0 e^{a\tau}}{c} U(r, t) \quad (15)$$

It is worth noting the physical reason for this simple result.  $U(r, t)$  is the temperature distribution due to an instantaneous spherical volume source at  $t = 0$ . Since our source,

$$\frac{Q}{c} n(\rho, \tau) = \frac{Qn_0}{c} e^{a\tau} U(\rho, \tau)$$

has the value of  $U$  at time  $\tau$  (except for the factor  $e^{a\tau}$ ), it follows that it will have the same value as  $U$  at any later time.

<sup>1</sup> The following definite integrals are involved

$$\begin{aligned} \int_{-\infty}^{\infty} \operatorname{erf}(a + bx) e^{-x^2} dx &= \sqrt{\pi} \operatorname{erf}\left(\frac{a}{\sqrt{1+b^2}}\right) \\ \int_{-\infty}^{\infty} \operatorname{erf}(a + bx) x e^{-x^2} dx &= \frac{be^{-a^2/(1+b^2)}}{\sqrt{1+b^2}} \end{aligned}$$

These can be established as follows: Let

$$\begin{aligned} I(a, b) &= \int_{-\infty}^{\infty} \operatorname{erf}(a + bx) e^{-x^2} dx \\ \frac{\partial I}{\partial a} &= \frac{2}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-(a+bx)^2 - x^2} dx = \frac{2}{\sqrt{\pi}} e^{-a^2/(1+b^2)} \int_{-\infty}^{\infty} e^{-\left(\sqrt{1+b^2}x + \frac{ab}{\sqrt{1+b^2}}\right)^2} dx \\ &= \frac{2}{\sqrt{1+b^2}} e^{-a^2/(1+b^2)} \end{aligned}$$

Then,

$$I(a, b) = \sqrt{\pi} \operatorname{erf}\left(\frac{a}{\sqrt{1+b^2}}\right) + f(b)$$

but  $I(0, b) = 0$ , since

$$\int_{-\infty}^0 \operatorname{erf}(bx) e^{-x^2} dx = - \int_0^{\infty} \operatorname{erf}(bx) e^{-x^2} dx$$

so that  $f(b) = 0$ . Similarly for the other integral.



From equation 10 there results

$$V(r, t) = \frac{Qn_0}{c} \frac{e^{\alpha t} - 1}{\alpha} U(r, t) \quad (16)$$

and finally, from equation 8

$$T(r, t) = T_0 + \left( T_1 - T_0 + \frac{Qn_0}{c} \frac{e^{\alpha t} - 1}{\alpha} \right) U(r, t) \quad (17)$$

giving the desired temperature distribution.

#### CONDITION FOR IGNITION

To obtain the condition for ignition, consider the temperature at the origin

$$T(0, t) = T_0 + \left( T_1 - T_0 + \frac{Qn_0}{c} \frac{e^{\alpha t} - 1}{\alpha} \right) \left( \operatorname{erf} \frac{R}{2\mu\sqrt{t}} - \frac{R}{\mu\sqrt{\pi t}} e^{-R^2/4\mu^2 t} \right) \quad (18)$$

This changes with time at the rate

$$\begin{aligned} \frac{\partial T(0, t)}{\partial t} = & - \left( T_1 - T_0 + \frac{Qn_0}{c} \frac{e^{\alpha t} - 1}{\alpha} \right) \frac{R^3}{4\sqrt{\pi} \mu^3 t^{5/2}} e^{-R^2/4\mu^2 t} \\ & + \frac{Qn_0}{c} e^{\alpha t} \left( \operatorname{erf} \frac{R}{2\mu\sqrt{t}} - \frac{R}{\mu\sqrt{\pi t}} e^{-R^2/4\mu^2 t} \right) \quad (19) \end{aligned}$$

To determine the relation which holds between the physical constants when

$$\frac{\partial T(0, t)}{\partial t} \geq 0$$

put

$$x = \frac{R}{2\mu\sqrt{t}}$$

$$\alpha = m \left( \frac{2\mu}{R} \right)^2$$

$$A = \frac{4(T_1 - T_0)k}{Qn_0 R^2} \quad (k = \text{thermal conductivity} = \mu^2 c)$$

then,

$$\frac{\partial T(0, t)}{\partial t} = \frac{2Qn_0}{c} x^5 e^{-x^2} \left[ -A - \frac{e^{m/x^2} - 1}{m} + \frac{e^{\frac{m}{x^2} + x^2}}{x^5} \left( \frac{\sqrt{\pi}}{2} \operatorname{erf} x - x e^{-x^2} \right) \right] \quad (20)$$

The function

$$F(x) = \frac{e^{\frac{m}{2x^2} + x^2}}{x^5} \left( \frac{\sqrt{\pi}}{2} \operatorname{erf} x - x e^{-x^2} \right) - \frac{e^{\frac{m}{2x^2}} - 1}{m}$$

approaches  $+\infty$  as  $x$  approaches 0 or  $\infty$  for  $m > 0$ . By differentiation it is found that  $F(x)$  has a single minimum given by the following relation between  $x$  and  $m$ .

$$m = x^2 \left[ x^2 \left( \frac{\operatorname{erf} x + \frac{2}{\sqrt{\pi}} x e^{-x^2}}{\operatorname{erf} x - \frac{2}{\sqrt{\pi}} x e^{-x^2}} \right) - \frac{5}{2} \right] \quad (21)$$

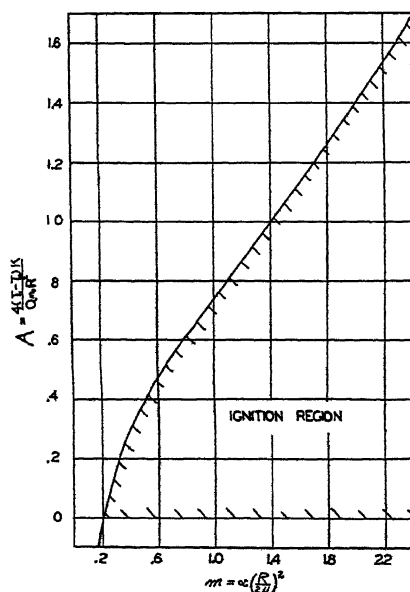


FIG. 2. Condition for ignition

From this there can be found the value of  $x$  which makes  $F(x)$  a minimum for a given  $m$ , and then the value of  $F(x)$  for this minimum. If  $A$  is not greater than this value, then from equation 20,

$$\frac{\partial T(0, t)}{\partial t} \geq 0$$

for all  $t$ .

This then gives the desired relation which must be fulfilled for a non-decreasing temperature at the origin. It is that

$$A = \frac{4(T_1 - T_0)k}{Qn_0R^2}$$

must be less than or equal to a value depending on  $\alpha$ , since  $m$  is merely  $\alpha$  expressed in convenient units. The ignition limit is, of course, given by the equality in this relation.

Figure 2 is a graph of the relation between  $A$  and  $\alpha$ , and figure 1 shows the course of the temperature at the origin for five pairs of values of  $A$  and  $\alpha$ .

#### SIGNIFICANCE AND APPLICABILITY OF THE THEORY

Unfortunately the result obtained in the last section cannot be tested by direct comparison with experiment, because the quantities which enter have not been measured in experiments on the ignition of gases. In fact, they may be incapable of direct experimental determination. However, certain conclusions can be drawn from this theoretical result as it stands, and it should be possible to perform experiments which will give some information about the needed quantities.

From figure 2 it can be seen that ignition does not occur if  $\alpha = 0$ ; that is, chain branching must take place for ignition to occur. This could have been expected to follow from the physical assumptions; because if the active particles do not increase in number, they eventually become very thinly spread out owing to diffusion and cannot generate enough heat to cause much rise in temperature. According to von Elbe and Lewis (8) the chain-branching reaction in the oxidation of hydrogen is negligible at low temperatures. Our conclusion would then be that ignition of a hydrogen-oxygen mixture by a local source can only occur if the source raises some volume to a high enough temperature for branching to be significant. This statement sounds very similar to those made by the proponents of a thermal theory of ignition. However, it is obvious that our theory does not state that ignition is assured by merely raising some volume to a sufficiently high temperature. The statement above is simply a limitation in the case where branching is known not to occur at low temperatures.

There is one set of experimental data which, though not exactly fitting the conditions assumed here, can be shown to give at least qualitative agreement with the theory. Silver (6) has studied ignition by shooting heated spheres of platinum and quartz into gases. He gives the minimum temperature to which spheres of various sizes must be heated to cause ignition in mixtures of 10 per cent coal gas, 3 per cent pentane, and 20 per cent hydrogen, each in air.

It is possible to relate Silver's experimental data to the considerations of this paper as follows. From figure 1 the condition for ignition is that

$$A = \frac{4(T_1 - T_0)k}{Qn_0R^2}$$

have a value which depends on

$$m = \frac{R^2}{4\mu^2} \alpha$$

The relation between  $A$  and  $m$  is, over a considerable range, close to a straight line passing through the origin, so that

$$A = \text{constant} \times \frac{R^2}{4\mu^2} \alpha$$

is the ignition relation. Now  $\alpha$  depends on temperature according to

$$\alpha = \text{constant} \times e^{-\frac{E_1}{RT}}$$

also  $Q$ , being proportional to a reaction rate follows a similar relation,

$$Q = \text{constant} \times e^{-\frac{E_2}{RT}}$$

The initial concentration of active particles probably depends on a surface reaction and can, therefore, also be assumed to be proportional to  $e^{-\frac{E_3}{RT}}$ . Then

$$\frac{T - T_0}{R^4} = \text{constant} \times e^{-\frac{E_1 + E_2 + E_3}{RT}}$$

and the graph of  $\log \left( \frac{T - T_0}{R^4} \right)$  against  $\frac{1}{T}$  should be a straight line. This graph is shown in figure 3 and it can be seen that the experimental values satisfactorily approximate a straight line.

The variation of  $k$  and  $c$  with temperature has been neglected. Inclusion of this factor would make no real difference in the appearance of figure 3; the slopes of the lines would be slightly increased.

Silver gave a theoretical discussion of his work, using as a criterion for ignition the requirement that the initial rate of heat production by the reaction shall be greater than the rate of heat loss by conduction. This led to the conclusion that the graph of  $\log \frac{T - T_0}{R}$  against  $\frac{1}{T}$  should be a straight line with a slope equal to the activation energy of the reaction.

The experimental points fell as close to straight lines as in the present analysis, but the slopes of the lines were approximately equal, whereas pentane and hydrogen have very different activation energies. The slopes of our lines are also not very different, but this is not contrary to the theory, since they should be proportional to  $E_1 + E_2 + E_3$ .

In the experiments just discussed,  $T_1$ , the initial temperature of the sphere, was determined directly. This is one of the quantities needed to test the theory, but in the case of an electric discharge it appears to be impossible to relate  $T_1$  to measured quantities. This suggests that it might be worth while to perform experiments with an energy source that released a known amount of energy, perhaps something like a percussion cap. It should then be possible to make statements about  $T_1$ . This

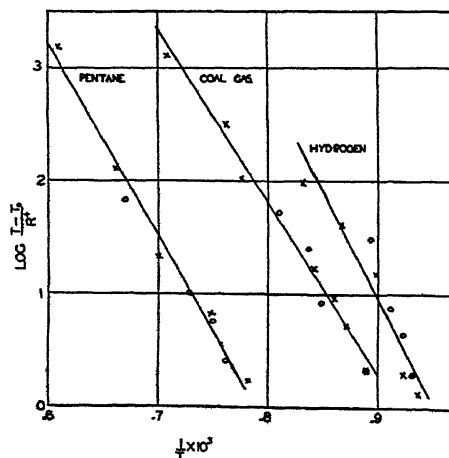


FIG. 3. Data of R. S. Silver (6) on ignition of gases by heated spheres. Experimental values: X, platinum spheres; O, quartz spheres.

would be of value not only for testing the present theory, but should also put an end to the controversy over the thermal theory of ignition by giving a direct answer to the questions involved.

To test the present theory it is also necessary to have information about  $n_0$ , the initial concentration of chain carriers. This requires a knowledge of the kinetics of the reaction and of the physical mechanism of the creation of these initial chain carriers.

If such information were available, it would be possible to make statements such as the following. Suppose  $T_1$  is held constant, then for a given mixture  $\alpha$  and  $Q$  should be constant. Let  $R$  and  $n_0$  vary, then from

$$\frac{4(T_1 - T_0)k}{Qn_0R^2} = \text{constant} \times \frac{R^2}{4\mu^2} \alpha$$

a relation of the form,  $n_0R^4 = \text{constant}$ , follows.

Again, if  $T_1$  is constant and pressure,  $p$ , and  $R$  vary, a relation between  $p$  and  $R$  is obtained. The form of the relation depends on the kinetics of the reaction. Suppose that chain branching,  $\alpha$ , requires the collision of  $m_1$  molecules, that the heat-producing reaction involves  $m_2$  molecules, and that the creation of the initial active particles involves  $m_3$  molecules; then  $\alpha = \text{constant} \times p^{m_1}$ ,  $Q = \text{constant} \times p^{m_2}$ ,  $n_0 = \text{constant} \times p^{m_3}$ . Also  $\mu^2$  is inversely proportional to density, hence inversely proportional to pressure. So that the relation is  $p^{m_2 + m_2 + m_3 + 1} R^4 = \text{constant}$ .

If the theory could be verified for reactions for which the kinetics is fairly well established, it should be useful to test hypotheses about the mechanism of other reactions.

#### SUMMARY

When energy is released by a local source such as an electric spark in a combustible gaseous mixture, it is assumed to heat instantaneously a small volume and also to create active particles, chain carriers, which diffuse through the gas and increase in number by chain-branching processes at a rate proportional to their concentration. The heat-producing reaction proceeds at a rate proportional to concentration of active particles. Taking as a criterion for ignition the requirement that the temperature at the point of ignition shall never decrease, the following condition for ignition is obtained:

$$A = \frac{4(T_1 - T_0)k}{Qn_0R^2}$$

must be less than or equal to a value depending on  $\alpha$ , the relation being given in figure 1.

The significance and applicability of this result are discussed.

This problem was suggested by Guenther von Elbe and Bernard Lewis. The author gratefully acknowledges his indebtedness to them and to M. A. Mayers of this laboratory for many helpful suggestions during the course of the work.

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*DISCUSSION<sup>2</sup>*

LOUIS S. KASSEL (Universal Oil Products Company, Chicago, Illinois): This paper certainly represents an interesting attempt to provide a mechanism for this important process. It may be worth while, however, to point out one feature of Landau's treatment that is perhaps oversimplified.

This is the assumption that the branching rate is independent of temperature; this admittedly incorrect proposition is justified by the statement that "the question as to whether ignition takes place or not is decided within a very short time." Inspection of figure 1, however, shows that when ignition fails the temperature at the origin may have risen, owing to the reaction, by 20 to 50 per cent as much as it had owing to the local source. Thus it is apparently required to assume that the branching rate is constant over a temperature interval of something like 100°C. It is to be expected that a theory which assumes a reasonable temperature coefficient for the branching rate will give a more rapid determination of whether ignition is to occur, and that failure to ignite will be preceded by only slight temperature rises. Even for these intervals, however, the increase of branching rate with temperature seems an essential feature of the theory, since it is only the effect of this increase which limits the abortive rise to a range over which one might think the branching rate could be considered constant.

<sup>2</sup> Received September 17, 1937.

## IGNITION REGIONS OF HYDROCARBONS

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### INTRODUCTION

Until comparatively recently any experimental evidence that the influences of such factors as varying temperature, pressure, or dilution on chemical reactions were other than in accord with simple laws would have been received by chemists with reserve, yet today many such apparent anomalies are recognized and their frequent occurrence in elementary combustion processes has contributed much evidence largely drawn upon in the development of the theory of chain reactions.

It is not surprising, therefore, that investigations into the combustion of complex hydrocarbons, designed in the first place to throw light on the problem of "knock" in internal-combustion engines, have shown when extended over wide enough temperature and pressure ranges that the mechanisms involved are far from simple; for such combustions are known to give rise to a variety of intermediate oxidation products, the concentrations of which at any stage of the reaction depend upon temperature, pressure, mixture composition, and environmental influences (cf. Newitt and collaborators (19, 17, 21, 18, 20)).

Systematic work on the influence of reaction temperature on the slow combustion of the higher paraffins, etc., in admixture with air was first published in 1929 by Pope, Dykstra, and Edgar (27, 2, 8) who, working in a flow system, established that, although initial oxidation commenced at 150–200°C., becoming active between 250°C. and 270°C. in which range the products were luminescent and then mildly explosive (cool flames) between 270°C. and 300°C., at higher temperatures the combustion was less rapid until about 500°C. had been reached. Parallel observations were also made by Pease (24, 26, 25), and a temperature range in which a negative temperature coefficient of reaction velocity occurred became recognized. Edgar also produced strong evidence that with straight-chain paraffins the methyl group at the end of the chain was first attacked with the formation of the corresponding aldehyde and water, the aldehyde being subsequently oxidized to a lower aldehyde, etc.; with side-chain isomers the same process occurred until the side chain was reached, when



a ketone was formed, and since ketones oxidize more slowly than aldehydes the reaction was slowed down, the luminescent combustion being less intense.

About the same time the cool-flame phenomena were examined by Emeleus (10), who showed the emission from several combustibles to exhibit spectra which differed from that of their normal flames but had a series of bands in common, recently identified as due to energized formaldehyde (cf. Ubbelohde (36) and Konratjew (14)). Prettre (28) also studied the character of the cool flames observed with many combustibles in a flow system. They were not observed with methane and ethane; rich mixtures of propane, pentane, hexane, heptane, and octane gave rise to them in a temperature range usually between 230°C. and 300°C., above which normal inflammation did not occur until about 600°C. had been reached. Aldehydes and ether readily exhibited cool flames, but amylene and amyl alcohol were the simplest olefin and alcohol, respectively, to give rise to them.

In 1933 Townend and Mandlekar (35), while studying the influence of pressure on the slow combustion of butane-air mixtures in a static system, observed that although at low pressures spontaneous ignition did not occur below 500°C., on the attainment of a critical pressure which varied somewhat with mixture composition it occurred abruptly in a temperature range below about 370°C., which was later recognized as that in which only cool flames are normally observable. The matter was therefore systematically investigated and extended to cover a wide range of combustibles.

The determination of ignition points over wide ranges of pressure and temperature, with which this paper is concerned, has been very fruitful in throwing light on the whole problem, for they provide information of the precise circumstances in which a maximum reaction velocity may be obtained under variable experimental conditions. It is now proposed briefly to review the field which has been covered so far and to indicate the general direction in which the results are leading, more detailed discussions of the possible chemical mechanisms involved being embodied in other papers contributed to this symposium.

#### IGNITION REGIONS OF THE PARAFFINS

In figure 1 curves have been drawn showing the influence of pressure on the ignition points of corresponding rich mixtures with air of methane, ethane, propane, butane, and hexane (curves 1, 2, 3, 4, and 5). The curve for the methane-air mixture fell rapidly from above 700°C. to about 500°C. as the pressure was raised to 5 atm.; thereafter it fell progressively to about 460°C. with increase of pressure to 30 atm. Similar curves have been obtained with other mixture compositions, that exhibiting the lowest

ignition points having a methane content between 30 to 40 per cent ( $\text{CH}_4:\text{O}_2$  ratio = 2:1). The intermediate products normally found in the slow combustion of methane are methyl alcohol and formaldehyde; the characteristics of the ignition point curves of both these materials are much the same as found with methane, but the order of ease of ignition is formaldehyde > methyl alcohol > methane, and small additions of formaldehyde strongly promote the combustion of the other two combustibles (12, 5).

With the ethane-air mixture (No. 2) at pressures up to 15 atm. the curve was as found with methane, ignition now occurring at somewhat lower temperatures. At this pressure (and at about  $430^\circ\text{C}.$ ) a sharp inflection

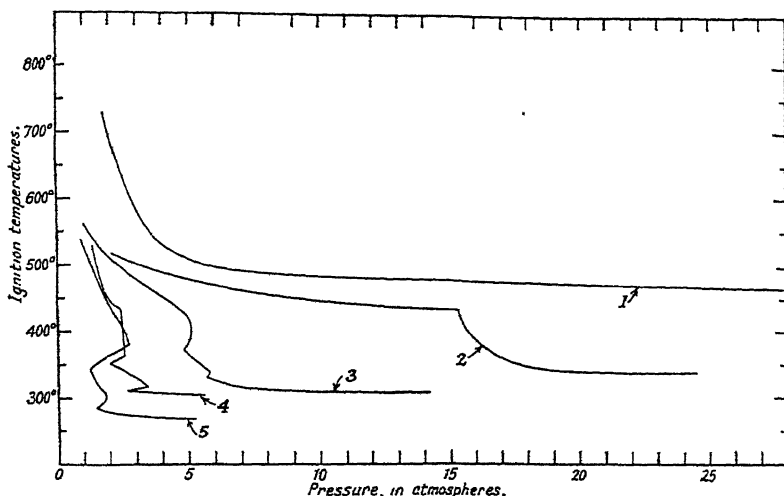


FIG. 1. Curves 1, 2, 3, 4, and 5 are for 13 per cent of methane, 10 per cent of ethane, 5 per cent of propane, 3.8 per cent of butane, and 2.7 per cent of hexane, respectively, in air.

occurred, the ignition points following an imposed lower system, settling down to temperatures about  $325\text{--}340^\circ\text{C}.$  at 25 to 30 atm. Another interesting feature of the experiments was the very long preignition time-lags recorded, for, whereas with methane these had increased progressively from 3 to 40 sec. with fall in ignition temperature to about  $460^\circ\text{C}.$ , with ethane the increase was from 20 sec. at  $550^\circ\text{C}.$  to a few minutes at  $435^\circ\text{C}.$ , the point of inflection; thereafter the lengthening was very marked and at  $325\text{--}340^\circ\text{C}.$  the lags had reached two *hours* or more.

With two carbon atoms in the molecule the number of intermediate compounds known in the intermediate products is greater than with methane, and it was thought not unlikely that at lower temperatures the



acetaldehyde-air mixtures (No. 3) left little doubt that the formation of acetaldehyde was responsible for the characteristic curves of ethane and ethyl alcohol, for at temperatures above about 330°C. a strong negative temperature coefficient of reaction velocity was apparent, a "throw back" in the ignition point curve being observed. It should also be mentioned that cool flames were observed for the first time with acetaldehyde-air media, and that they occurred within the temperature and pressure limits defined approximately by the dotted boundary curve enclosing the shaded area. When true ignition occurred in this temperature range at an adequately high pressure (defined by curve 3), it always followed at a definite short time interval following the formation of a cool flame. The simplest interpretation of these results would seem that at the upper temperature limit of the lower system the life of intermediately formed acetaldehyde is inadequate to promote the combustion as a whole; it may equally well be, however, that this applies to some product to which the aldehyde gives rise or, alternatively, that some other process sets in which renders the aldehyde innocuous; pending further chemical evidence, however, judgment should be suspended.

Reverting again to figure 1, curves 3, 4, and 5, pertaining to propane-, pentane-, and hexane-air mixtures, it will be observed that with all paraffins containing three or more carbon atoms an abrupt fall in the ignition points occurred, an important observation being the occurrence of two pressure minima of ignition, one at about 280–330°C. and the other at about 340–370°C., both being lowered progressively as the hydrocarbon series was ascended. These observations have recently been extended by Mr. M. Maccormac in these laboratories to cover heptane, octane, and decane, with results which are in conformity with the behavior of the lower members of the series.

It is also important to note that as the series was ascended not only did the minimum pressures for ignition in the lower range decrease, but the preignition time-lags were also materially reduced; for instance, with propane lags of the order of 3 to 5 sec. were reduced to less than 1 sec. with hexane.

With members containing three or more carbon atoms there were also fairly well defined pressure and temperature limits within which cool flames were propagated, those for three propane-air mixtures containing 2.6, 5.0, and 7.5 per cent of the combustible being illustrated by the diagonally shaded areas associated with the ignition point curves, Nos. 1, 2, and 3 in figure 3. When cool flames were propagated a slow-moving, pale bluish flame was observable through the windows provided in the explosion vessel; this was accompanied by the development of a small pressure pulse and a considerable formation of intermediate compounds

strongly aldehydic in character. The phenomenon was quite different from normal flames which are usually fast travelling, giving rise to a whitish emission and high pressure development, the products containing only traces of intermediate compounds. As will be shown later the cool flames occurred after a definite time-lag which was usually of the order of 20 to 30 sec. at the lower temperature boundary; as at any selected pressure the temperature was raised, these lags were appreciably shortened and the cool flames became more intense up to about  $360^{\circ}\text{C}$ . Above this temperature the lags became very short and the intensity of the flames rapidly diminished, until above the upper temperature limit they were no

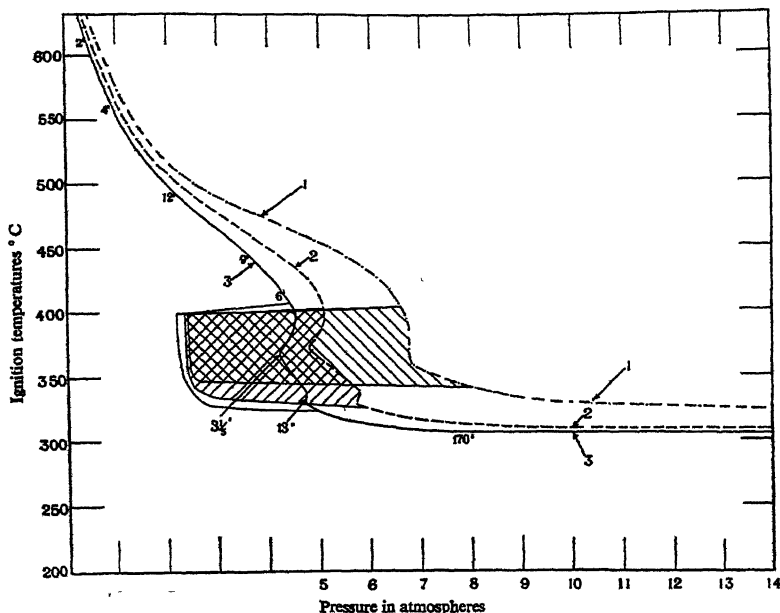


FIG. 3. Propane-air mixtures. Percentage mixtures for the curves: curve 1 = 2.6; curve 2 = 5.0; curve 3 = 7.5

longer observable. At a stated temperature the cool flames also increased in intensity as the pressure was raised from the lower pressure limit; and when a pressure adequate for true ignition was attained a two-stage process occurred, the full ignition following rapidly after the formation of a cool flame. Such behavior may be regarded as characteristic of all the higher paraffins.

It should perhaps be stated here that the method employed in the determinations so reviewed was that which originated with Mallard and Le Chatelier, the mixture under investigation being admitted rapidly into an evacuated vessel maintained at the experimental temperature; the vessel

employed had a cylindrical cavity 17 cm. x 3.75 cm., capacity = 170 cc., and was provided with a mild-steel liner. If liners of other materials were employed, ease of ignition seemed to depend on their catalytic inactivity; moreover, alteration in the dimensions of the cavity, while influencing the precise location of the curves according to circumstances, was without effect on the general character of the phenomena. Owing to the extreme violence of the ignitions usually found when undiluted combustible-oxygen mixtures were employed (particularly with those containing excess of oxygen) and also because a main interest has been in correlating ease of spontaneous ignition under pressure with the known "knocking" propensities in engine practice of the fuels concerned, the investigations so far completed have been mainly restricted to mixtures made with air. Recently, however, Newitt and Thornes (22) have made a close examination both of the ignition characteristics of an equimolecular propane-oxygen mixture in silica vessels and also of the intermediate products at all stages of the combustion, which has thrown further light on the subject; of particular interest has been their observation that in certain circumstances it is possible for as many as five cool flames to succeed one another. Elsewhere, Neumann and his collaborators (1) and Prettre (29) have studied the behavior in the cool-flame regions of mixtures of butane and pentane with oxygen, their observations agreeing in all essentials with those already described but being more directed towards their kinetic interpretation.

#### THE RELATIONSHIP BETWEEN SPONTANEOUS IGNITION AND KNOCK

It is now generally recognized that the behavior of any fuel in an engine is largely influenced by the chemical reactivity of the unburnt medium ahead of the flame (cf. 9, 37, 38, and 30), this being controlled by the degree of compression, the working temperature, and speed of running. In such circumstances where the available time interval is short any *appreciable* chemical reaction must *ipso facto* be intense, and conditions will approximate closely to those of the ignition point; indeed, since the work of Tizard and Pye (33) it has been well appreciated that there is in general a close relationship between both ignition points and temperature coefficients of reaction velocity of fuel-air media and their knocking propensities in an engine. There have been, however, certain practical difficulties to an unqualified acceptance of this relationship; also, although it was early recognized that a limit was set to engine design by critical compression ratios depending on the fuel employed, the part played by pressure other than by raising the working temperature remained obscure, there being no reason to suppose that its influence on ignition points was abnormally great and other than quite progressive.

When it was discovered with the higher paraffins that (1) the lower ignition region approximated to the ordinary compression temperatures attained in an engine, (2) ignition occurred abruptly in this region with a minimum time-lag on the attainment of a critical pressure, while at higher temperatures the mixtures were non-ignitable, (3) mixtures rich in combustible ignited at a lower critical pressure than those containing excess of air, (4) not only did ignition occur at progressively lower pressures as the series was ascended but the time-lags were also materially reduced, and (5) the presence of an antiknock raised the pressure necessary for ignition, it became clear that it was to the pressure requisite for ignition in the lower range that the standard knock ratings of fuels were probably related.

In considering the ignition point determinations in the light of their probable application to internal-combustion engines, however, the question of time-lag was of predominating importance, because in such conditions the maximum lag permissible would not exceed a few thousandths of a second. It is not possible with the method of working in the investigations described herein to determine with precision lags of much less than 0.5 sec. Propane-air mixtures, however, while exhibiting the behavior characteristic of the higher paraffins generally, have much longer time-lags than found with the higher members, so that it was possible to indicate the general influence of pressure on them.

In figure 4, curve 1 shows the ignition points of a 7.5 per cent propane-air mixture plotted against pressure in the ordinary way; the lags printed against the curve were those at these minimum ignition pressures and as previously pointed out they were variable, being usually shortest in the cool-flame temperature range. The figures in the cool-flame area are the lags observed at 360°C. and 370°C. prior to the appearance of a cool flame; they decreased with increase of pressure and corresponded with the lags observed for true ignition when the requisite pressure had been attained.<sup>1</sup> The temperature of minimum lag on curve 1 was found at about 370°C.; at higher and lower temperatures on the curve this lag increased, but by increasing the pressure above the minimum the lags were shortened. Curve 2 is the curve so plotted for ignition with a lag of 3.2 sec. Similarly, curves 3, 4, and 5 were plotted for lags of 2, 1, and 0.6 sec., respectively.

Marked pressure minima persist in the iso-lag curves at higher pressures, an interesting feature being that the temperatures at which the minima are located do not remain fixed but show an immediate sharp rise from 370°C. to 415°C., thereafter apparently remaining constant; this tempera-

<sup>1</sup> Cf. inset, figure 4. When true ignition occurred the lags showed a slight increase due to the two-stage process already referred to. The dotted curve shows the lags for the same mixture, but with an addition of 0.05 per cent of lead tetraethyl.

ture corresponds with the upper limit for cool flames. Also when the time-lags become short by increasing initial pressure the ignitions are extremely violent and akin to detonation, a matter which is being further investigated by Dr. G. P. Kane in these laboratories.

With higher hydrocarbons (cf. hexane (34)) an iso-lag curve of the type shown by No. 5, figure 4, would relate to extremely short lags, immeasurable without special methods; and when it is recalled that the compression temperature of the working fluid in an engine varies with the compression ratio employed somewhat as follows: 4:1, 385°C.; 5:1, 410°C.; 6:1, 430°C. (although in engine practice other factors such as dilution with explosion

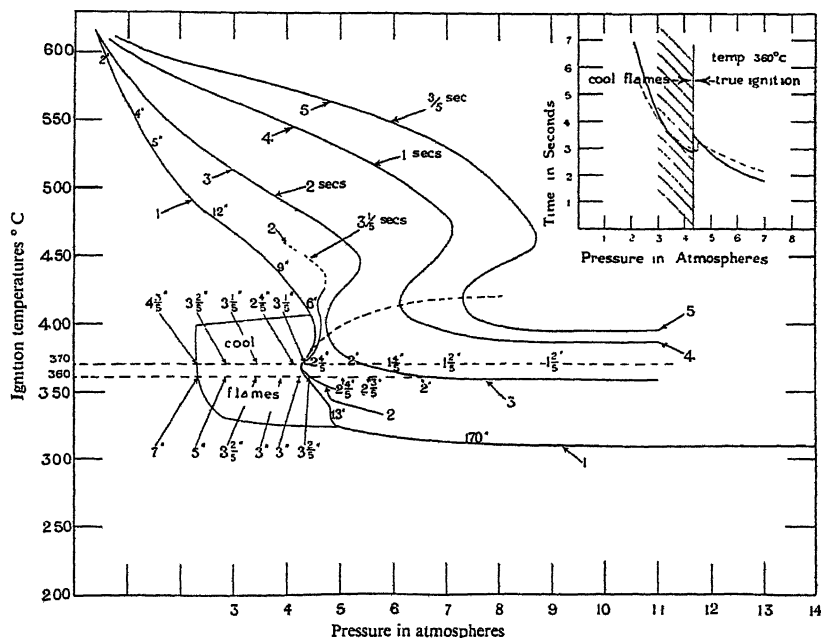


FIG. 4. Influence of pressure on time-lags. 7.5 per cent propane-air mixture

products, the formation of reaction centers during the compression stroke, and the part played by the advancing flame call for consideration), there would seem little doubt at all as to the general significance of the curves. Incidentally also it is clear why slow running is conducive to knock for, although this has been attributed in some quarters to better volumetric efficiency, it is more likely due to the increased available lag period.

While so far we have confined this discussion to the straight-chain paraffins, it remains to state that no exception has yet been found to the relationship between knocking propensity of any fuel and the pressure requisite at the compression temperature for its spontaneous ignition



within a short time-lag. Thus the knock ratings of ethane, ethyl alcohol, and acetaldehyde (14.0, 7.5, badly knocking) would be inferred at a glance from the curves in figure 2. To illustrate the behavior of side-chain paraffins, in figure 5A the ignition point curves of corresponding mixtures with air of butane, isobutane, and iso-octane (2,2,4-trimethylpentane) have been drawn (curves 1, 2, and 3). Figure 5B contrasts the behavior of mixtures of hexane and cyclohexane (curves 1 and 2). Materials such

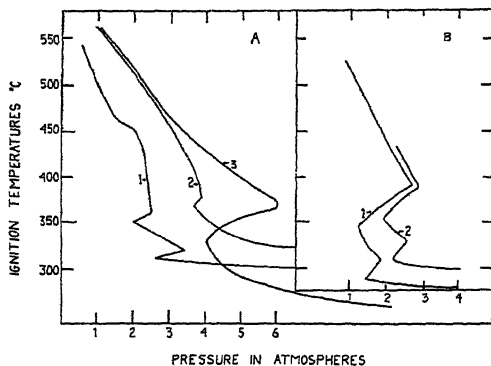


FIG. 5. (A) Theoretical mixtures with air of butane (curve 1), isobutane (curve 2) and iso-octane (curve 3). (B) Theoretical mixtures with air of hexane (curve 1) and cyclohexane (curve 2).

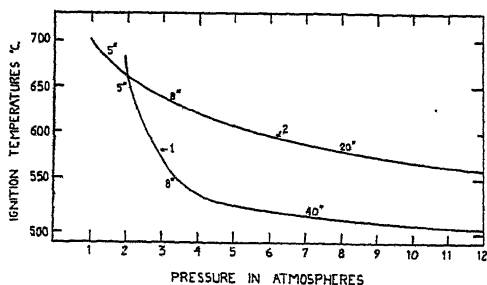


FIG. 6. Theoretical mixtures with air of methane (curve 1) and benzene (curve 2). Small figures along the curves denote time-lags.

as methane and benzene (11), which do not knock, exhibit ignition point curves which apparently show no lower system at all (curves 1 and 2 in figure 6). The behavior of the simpler olefins will now be described.

#### IGNITION REGIONS OF THE SIMPLER OLEFINS

Recently Kane and Townend (13) published an account of an extension of the investigations into the influence of pressure on the spontaneous ignition of hydrocarbon-air media to the simpler  $\alpha$ -olefins,—ethylene, propylene, butylene, and amylene. In figure 7, curves 1, 2, and 3 show

the influence of pressure on the ignition points of theoretical mixtures with air of ethylene, propylene, and butylene.

With the ethylene mixture (No. 1) the ignition points fell progressively with increase of pressure, a smooth curve of the type previously observed with methane-air mixtures being obtained. There was never any indication of the formation of cool flames, even though the curves for rich mixtures fell to about 300°C. at sufficiently high pressures, nor was any irregularity in the time-lags observed; these increased from 4 to 5 sec. at 550°C. to about 30 sec. at 370°C. and 240 sec. at 310°C., varying slightly with mixture composition.

The fact that the ignition point curves for ethylene-air mixtures are quite smooth and that no superposed lower system as found with ethane-air mixtures was observed is a matter of interest, because, as has already been pointed out, strong evidence was adduced that with ethane this

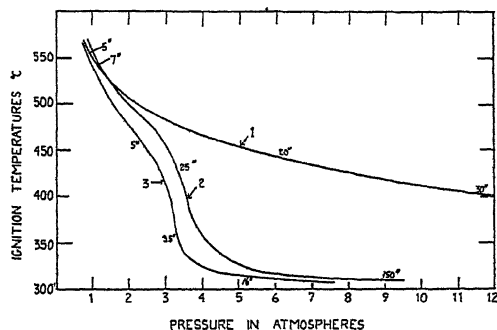


FIG. 7. Theoretical mixtures with air of ethylene (curve 1), propylene (curve 2), and butylene (curve 3). Small figures along the curves denote time-lags.

was attributable to an adequate formation of acetaldehyde, which is a principal product in its slow oxidation. If this be correct it seems possible that the known formation of acetaldehyde in the slow combustion of ethylene (6, 15, 17) arises not as a direct immediate oxidation product but as the outcome of a slower secondary process less likely to influence ignition. This would be in agreement with the view that acetaldehyde arises by an isomeric change from a primary product (cf. Bone (4)) and also with Norrish's atom chain mechanism as applied to ethylene (23). Formaldehyde, on the other hand, which is known to promote the main combustion (6) was always a product of the preflame combustion and the curve is consistent with its playing such a rôle, as in fact it does with methane (cf. p. 261).

Pressure had a far more marked influence on the ignition points of the propylene-air mixture (No. 2). The ignition points fell progressively at the lower pressures to about 440°C.; further increase of pressure, however,

caused an abrupt fall over a temperature range where cool flames were also observable, but below about 330°C. increase of pressure had little further influence. Although the ignition points fell rapidly no irregularities in the time-lags were observed; in this respect and in the fact that the curves showed no pressure minima propylene differs from propane. A study of the respective behaviors of propane and propylene may better be made by comparing figure 8, which shows both the ignition point curves and the cool-flame areas for three propylene-air mixtures containing 3.0, 4.5, and 6.0 per cent of the combustible, with figure 3. The main difference, however, lay in the weakness both of the pressure pulses and of the luminosity associated with the cool flames of propylene, a fact which made

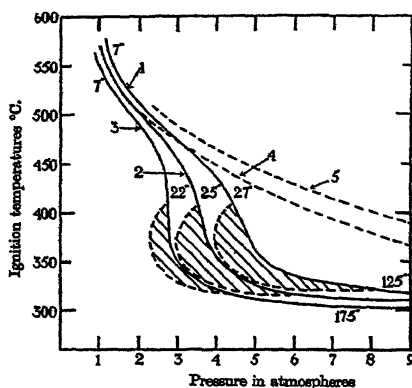


FIG. 8

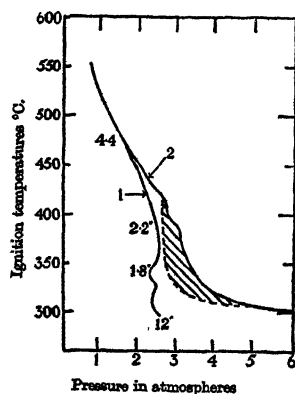


FIG. 9

FIG. 8. Propylene-air mixtures. Percentage mixtures for the curves: curve 1 = 3.0; curve 2 = 4.5; curve 3 = 6. Curves 4 and 5, for the 4.5 per cent mixture, relate to ignition with constant lags of 3 and 2 sec. Shaded areas indicate cool-flame regions.

FIG. 9. Amylene-air mixtures. Curve 1 = 2 per cent of  $\alpha$ -amylene; curve 2 = 2 per cent of isomeric amylenes.

impossible precise determinations of the pressure and temperature limits for them. Moreover, although for corresponding mixtures those with propylene were ignitable at slightly lower pressures than those of propane, not only were the time-lags longer with the former but their rate of decrease with increase of pressure was not as great; curves 4 and 5, in figure 8, relate to ignitions of the 4.5 per cent mixture No. 2 with a constant lag of 3 and 2 sec., respectively, and may be compared with the curves for a 7.5 per cent propane-air mixture (figure 4).

The ignition point curve for the  $\alpha$ -butylene-air mixture (No. 3, figure 7) resembled closely that obtained with the propylene-air mixture, the minimum ignition points, however, occurring at lower pressures. Al-

though there was still no indication of pressure minima of ignition in the lower temperature range characteristic of the higher paraffins, the lags, which were much shorter than those observed with either ethylene or propylene, showed an irregularity in this range as found with the paraffins; thus they were reduced from about 5 sec. at 450°C. to a minimum value of 3.5 sec. at 370°C., thereafter increasing to 16 sec. at still lower temperatures. The cool flames were also more pronounced in regard to both the accompanying pressure pulses and luminosity.

Amylene as supplied commercially (b. p. 36–40°C.) consists of side-chain isomers. A small quantity of  $\alpha$ -amylene (b. p. 30.3°C.) was specially synthesized, but only sufficient was available to complete the ignition point curve of a mixture containing 2 per cent of it (theoretical mixture,—2.7 per cent); this is shown in figure 9, No. 1. Other curves were determined with a sample of purchased material containing more stable isomers; No. 2 relates to a 2 per cent mixture of this material.

The ignition points of the  $\alpha$ -amylene mixture (No. 1) gave for the first time definite evidence of the pressure minima in the cool-flame temperature range, invariably found with the higher paraffins; the higher minima occurred at 340°C. and the lower at 312°C. The time-lags were also irregular as with the paraffins, a minimum value of 1.8 sec. being observed at 340–350°C. Cool flames were observable between 310°C. and 410°C., the pressure pulses being marked between 310°C. and 360°C. Moreover, as would be anticipated, the mixture of the side-chain isomers No. 2 was not nearly as easily ignitable as that of the  $\alpha$ -olefin.

#### COMPARISON OF THE RESPECTIVE BEHAVIORS OF PARAFFINS AND OLEFINS

From the results obtained with the four simpler olefins it may be stated that the influence of pressure on their spontaneous ignition in admixture with air is not unlike that found with the paraffins. Thus, ethylene behaves like methane, and although propylene and butylene did not reveal strong negative temperature coefficients of reaction as found with the corresponding paraffins, the ignition point curves exhibited a sharp fall over narrow critical pressure ranges to a lower system where cool flames were normally observed; and finally a 2 per cent  $\alpha$ -amylene-air mixture showed all the characteristics typical of higher paraffin-air mixtures.

Also the minimum pressures requisite for ignition in the lower temperature range with corresponding mixtures, considered in the light of the observed time-lags, indicate that the knock ratings of both olefins and paraffins should fall as the series is ascended. This is in accord with the "critical compression ratios" of Boyd, as table 1 shows. The results of the investigation as a whole are, in fact, in conformity with the general

conclusions of Boyd (16), that (1) in an homologous series, whether paraffinic or olefinic, the tendency to knock increases with increasing length of the saturated carbon chain, and (2) in an isomeric series, knock decreases progressively with the centralization of the double bond.

Reverting to the chemical processes operative in the combustion of either paraffins or olefins containing more than three carbon atoms, at least three conditions call for consideration: namely, (i) that giving rise to cool flames in the temperature range usually between about 280–410°C.; (ii) that ultimately resulting in true ignition in the products from cool flames, there being usually two distinct zones of activity, (a) 300–330°C. and (b) 340–370°C., respectively; and (iii) that occurring above the upper

TABLE 1

*Comparison between critical compression ratios and minimum ignition pressures*

HYDROCARBON	CRITICAL COMPRESSION RATIO (BOYD)	MINIMUM IGNITION PRESSURE AT 350°C.	TIME-LAG
		atm.	sec.
Olefins:			
Ethylene . . . . .	8.5		
Propylene . . . . .	8.4	5.0	30
$\alpha$ -Butylene . . . . .		3.35	3.5
$\alpha$ -Amylene . . . . .	5.8	2.4	1.8
Paraffins:			
Ethane . . . . .	14		
Propane . . . . .	12	6.8	3
Butane . . . . .	6.4	3.4	2
Pentane . . . . .	3.8	2.2	1.4
Hexane . . . . .	3.3	1.9	1
Isobutane . . . . .	8.9	4.4	3

limit for cool flames, i.e., above about 410°C. It would seem that with most fuels conditions conducive to (i) are mainly responsible for knock,<sup>2</sup> and that the phenomenon itself involves essentially the processes occurring in (ii) which are intense at sufficiently high pressures.

<sup>2</sup> This holds without doubt for fuels of "critical compression ratios" < 6 to 8. At higher compression ratios the compression temperature would doubtless approach 500°C., which is probably in the upper ignition range even with very short time-lags. It is significant that propylene (C. C. R. = 8.4) is the only olefin to exhibit a knock rating lower than that of the corresponding paraffin (C. C. R. = 12), and reference to figures 4 and 8 shows that whereas in the lower range the iso-lag curves for propane occur at much lower pressures than with propylene, in the higher range the reverse is true.

There is little doubt that the processes giving rise to cool flames are of a chain character and probably associated with the presence of higher aldehydes and other active intermediate bodies. That aldehydes are important intermediate products may be seen from figure 10, which shows the ignition points of a 7.5 per cent propane-air mixture, No. 1, which contains defect of air with which 1 and 2 per cent of propionaldehyde, Nos. 2 and 3, and 1 and 2 per cent of acetaldehyde, Nos. 4 and 5, had been admixed. The influence of acetaldehyde on the cool-flame area has also been illustrated. There is little difference in the behavior of the two

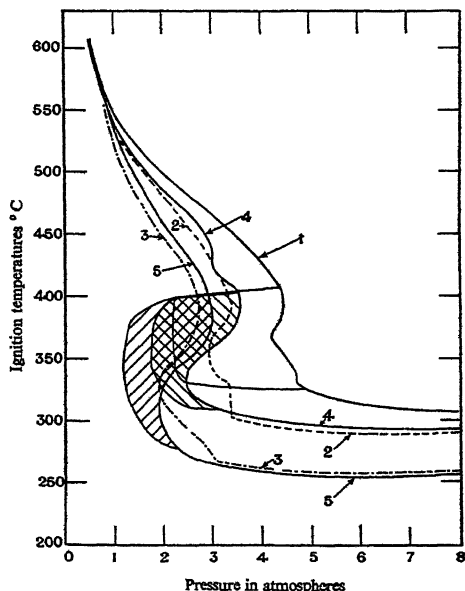


FIG. 10. Curve 1 = 7.5 per cent propane-air mixture; curves 2 and 3 = the same with addition of 1 and 2 per cent of propionaldehyde; curves 4 and 5 = the same with addition of 1 and 2 per cent of acetaldehyde.

aldehydes in facilitating ignition; both induce ignition in the lower temperature range at much lower pressures and temperatures than are observed with the simple mixture, and both have much less influence on the ignition points at higher temperatures and comparatively none above 550°C. A similar effect was also found on addition of 1 per cent of acetaldehyde to a 4.5 per cent propylene-air mixture.

While the behavior of the  $\alpha$ -olefins under pressure is not unlike that of corresponding paraffins, the main difference lies in the reduced luminosity of the cool flames and the feeble pressure pulses observed with them, indicating that the processes operative in the low-temperature system are less

intense than with the paraffins; moreover the preflame time-lags were not only greater but decreased less rapidly with pressure. There would seem no reason to postulate any difference in the intermediate products (or chain initiators) responsible for promoting reaction with both homologs, and these probably result from the formation of higher aldehydes. This view would be in agreement with the well-known researches of Beatty and Edgar (2). Kane and Townend (13) regarded the degenerate branching view of Semenoff (31) as attractive in explaining their results, for the less vigorous behavior of the olefins may be attributable either to a slower building up of active centers depending upon aldehyde concentration by virtue of difference in the chemical stages involved, or to the intervention of stronger inhibiting processes. The former explanation is readily interpretable by comparing the respective stages involved in building up higher aldehydes from propane and propylene (cf. 3, 23). With regard to the kinetics of the chain mechanisms involved, Aivazov and Neumann (1) have developed an empirical equation agreeing closely with experiment for the relation between the preignition time-lags for cool flames, which are regarded as ignitions giving rise to stable intermediate products, and the experimental temperature, pressure, vessel diameter, and minimum cool-flame pressure. Their expression is based on Semenoff's theory of spontaneous ignition as arising by a process of interacting chains in accordance with the expression

$$\frac{dn}{dt} = n_0 r - (g - f)n + f^1 n^2$$

where  $n_0$  = the number of active centers formed,  $r$  = the length of the primary chain,  $g$  = the chain-breaking factor,  $f$  = the chain-branching factor, and  $f^1 n^2$  takes account of chain interaction,  $f^1$  being small. No suggestions are made, however, as to either the character of the interacting centers or the products likely to be produced from them. Prettre (29) has also related the time-lags observed with pentane-oxygen mixtures with a simple chain mechanism.

No complete explanation has so far been forthcoming to account for the upper temperature limit for cool flames. Recent experiments on ether-air mixtures in these laboratories leave little doubt that the mechanisms operative are the same whether the flames are ignited artificially in cold media by means of a hot wire or whether they are developed spontaneously in a sufficiently heated vessel. It would appear that for some reason there is an upper temperature barrier to the flames which is never exceeded. This may possibly be due to thermal instability or elimination by other means of a chain initiator or material giving rise to a chain initiator; or it may also well be that an intermediate product (e. g., acetaldehyde) breaks

down by a chain process. From a thermal point of view the temperature restriction may perhaps be likened to the limitation imposed in high-temperature flames by the dissociation of carbon dioxide and water; an important clue would seem to be the presence in the flames of energized formaldehyde.

#### THE INFLUENCE OF NITROGEN DIOXIDE

Interesting light on the problem has recently been thrown by studying the influence of small amounts of nitrogen dioxide on the ignition points (13). In figure 11A the influence of successive additions of 0.1 and 1 per cent of nitrogen dioxide to a 7.5 per cent propane-air mixture (curve No. 1) may be seen from the corresponding ignition point curves (Nos. 2 and 3).

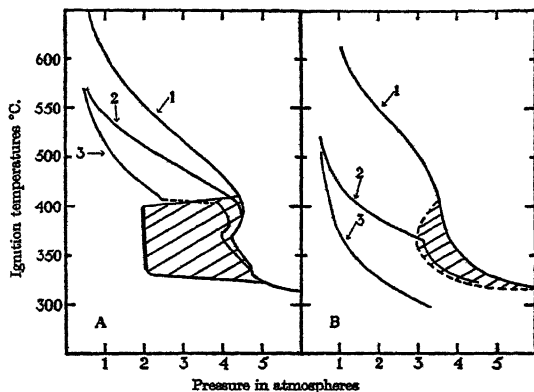


FIG. 11. (A) Curve 1 = 7.5 per cent propane-air mixture; curves 2 and 3 are the same but with 0.1 and 1.0 per cent additions of nitrogen dioxide. (B) Curve 1 = 4.5 per cent propylene-air mixture; curves 2 and 3 are the same but with 0.1 and 1.0 per cent additions of nitrogen dioxide.

By far the greatest influence of the promoter was not only to reduce the time-lags, but to effect ignition at much lower pressures in the temperature range above the upper limit for cool flames. There now appeared, in fact, an abrupt transition from the sensitized ignition typical of the upper system to ignition arising as a sequence of cool flame formation, as indicated by the dotted line (curve No. 3). Thus in the low-temperature range the presence of nitrogen dioxide had by comparison no great influence in extending the cool-flame limits, and the ignition limits while being slightly reduced at temperatures between about 330°C. and 400°C. were, if anything, raised at lower temperatures.

There was thus important and independent evidence of different chemical mechanisms in the two ignition ranges, and the results suggest the possibility of mutual destruction of active centers in the lower system. The



comparative ineffectiveness of nitrogen dioxide in promoting combustion in the cool-flame range is of great interest, because it is in keeping with the observation of Egerton and collaborators (9, 37) that it was without influence in inducing knock with butane, heptane, and petrol, although with hydrogen it did so.

In figure 11B a corresponding set of curves has been drawn showing the respective influence of addition of 0.1 and 1 per cent of nitrogen dioxide (curves 2 and 3) to a 4.5 per cent propylene-air mixture (curve 1). Apart from reduction in the time-lags the presence of nitrogen dioxide was still without influence on the limits within which cool flames were observed. With regard to true ignition, however, the presence of 0.1 per cent of nitrogen dioxide not only very greatly reduced the limiting pressures in the upper system but promoted ignition resulting in the lower system in the cool-flame products (curve 2); and 1 per cent of it so sensitized the com-

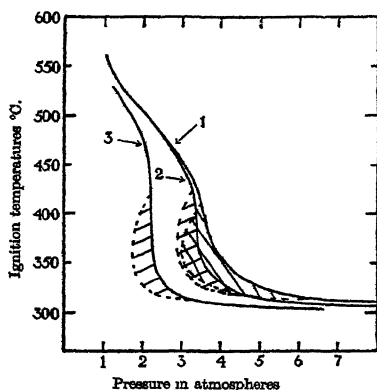


FIG. 12. Curve 1 = 4.5 per cent propylene-air mixture; curves 2 and 3 are the same but with 0.1 and 0.5 per cent additions of diethyl ether. Shaded areas indicate cool-flame regions.

bustion that a smooth curve (No. 3) was obtained, ignition occurring over the whole range without any apparent prior cool-flame reaction whatever. This marked difference in the relative influence of nitrogen dioxide in the lower system with propane and with propylene seems in agreement with the views already expressed concerning the two combustions, for the rate of chain development with propylene, which is by comparison with propane a slow process, would be the more enhanced by the addition of active centers to the system.

#### THE INFLUENCE OF ETHER

It is well known that ether vapor when added to a fuel-air mixture acts as a strong proknock. Newitt's recent discovery (20) of the forma-

tion of mixed ethers in the slow combustion of olefins has revealed another class of intermediate compounds, the influence of which calls for investigation. In figure 12, curves 2 and 3 show the influence of additions of 0.1 and 0.5 per cent of ether to a 4.5 per cent propylene-air mixture (No. 1). Ether plays a rôle rather like, but much more powerful than, that of acetaldehyde, for 0.1 per cent of it (No. 2), while facilitating combustion in the lower range below 425°C., was without influence at higher temperatures; an addition of 0.5 per cent of it (No. 3), however, powerfully promoted the combustion, this being marked even up to 500°C. So far as the matter has been tested a similar effect has been found with propane-air mixtures.

The interpretation of the respective influences of higher aldehydes, ether, and nitrogen dioxide on the combustion as described is now forming the subject of further investigation.

#### SUMMARY

Researches into the combustion of complex hydrocarbons, designed to throw light on the problem of knock in internal-combustion engines, have revealed generally that the mechanisms involved are far from simple. Much new light has recently been thrown on the subject by systematic investigation of the influence of pressure on the spontaneous ignition points of these materials.

Inflammable mixtures with air of the paraffins containing three or more carbon atoms, while not spontaneously ignitable at low pressures below about 500°C., give rise abruptly to ignition at higher pressures in a temperature range between about 310°C. and 370°C., where normally only "cool flames" are initiated; and although neither methane-air nor ethane-air mixtures appear to develop cool flames, the latter are ultimately ignitable in a lower temperature system less complex than that characteristic of the higher members. There is general agreement between ease of ignition in the lower temperature range and the knock ratings of the materials concerned. This holds good for side-chain paraffins, olefins, naphthenes, and aromatic fuels.

All olefins higher than ethylene behave in a similar manner; they differ from the paraffins in that the cool flames are less intense and the preflame time-lags are not only greater but decrease less rapidly with increase of pressure.

The influence of higher aldehydes, nitrogen dioxide, and diethyl ether as promoters of ignition is also discussed.

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## THE SLOW COMBUSTION OF GASEOUS PARAFFINS, ESPECIALLY PROPANE

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The non-explosive oxidation of gaseous paraffins, which occurs at about 300°C. and 1 atm., has as its outstanding characteristic a lengthy induction period. During the minutes or hours that this may take to complete itself, some infinitesimal alteration of the reaction system must be taking place. In his original work on ethane, Bone (2) limited himself to the suggestion that "the gases (or at least one of them) were merely 'getting ready' in some way." Later work on methane revealed that the reactants were not entirely inert during the induction period. Toward the end, small amounts of formaldehyde could be detected (1). This fact, coupled with the observation that the formaldehyde increases to a maximum at the maximum reaction rate and that added formaldehyde can eliminate the induction period, points inescapably to this substance as the active intermediate.

If one were to conclude that the function of the formaldehyde is to introduce active oxygen into the system either as atoms (3) or as peroxide oxygen (9), one might predict that higher aldehydes (e.g., acetaldehyde) would be even more efficient. This is, in fact, apparently just what has been observed in the case of ethane oxidation. Bone and Hill found, for example, that with 1 per cent of acetaldehyde at 316°C. explosion occurred. To be sure, this conclusion about active oxygen supplied by the aldehyde runs counter to the observation that potassium chloride largely eliminates peroxide oxygen without radically altering the rate of hydrocarbon oxidation (8). Nevertheless, the case is certainly a strong one, as von Elbe and Lewis have shown.

In view of the above, it was most surprising to find that acetaldehyde is by no means so efficient in inducing the oxidation of propane as it appears to be in the case of ethane. The experiments to be described in the following were undertaken to investigate the relation of the rate of oxidation of propane to the propane and oxygen concentrations. In order to obtain measurably low rates it was necessary to reduce the temperature somewhat below 300°C., but when this was done the induction period became exces-

sively long. To get around this difficulty small amounts of acetaldehyde vapor were introduced into the reaction bulb before the propane-oxygen mixture. The reaction was followed by pressure measurement.

It was found that with 300 mm. each of propane and oxygen at 280°C. in the uncoated reaction bulb, the induction period ( $\Delta P < 1$  mm.) was 39 min. and reaction was virtually completed in 5 min. more. When 20 mm. of acetaldehyde was first introduced into the reaction bulb a mild explosion occurred. With 2 mm. of acetaldehyde, there was a 6-min. induction period, after which reaction was again completed in 5 min.

Similar results were obtained after treating the reaction bulb with potassium chloride. At 280°C. and 300 mm. of each gas, the induction period lasted more than five hours. At 270°C. (10°C. lower) 20 mm. of acetaldehyde again caused inflammation. With 5 or 10 mm. of acetaldehyde, there was a 1- to 2-min. induction period followed by quiet reaction.

These results are evidently quite different from those obtained by Bone with formaldehyde and methane-oxygen, or acetaldehyde and ethane-oxygen. The induction period is not eliminated by aldehyde but only shortened, unless sufficient aldehyde is present to induce explosion, quite possibly as a purely thermal effect.

The writer inclines to the belief that the effect of acetaldehyde in this case is exerted on the surface. Since altering the surface (coating with potassium chloride) profoundly alters the induction period, the process of "getting-ready" (Bone) is clearly a surface process, as others have remarked. Since this process is only altered but not eliminated by acetaldehyde, this alteration should likewise be localized at the surface. The nature of the process in the presence or absence of aldehyde is by no means clear, but something in the nature of activated adsorption would seem to be indicated. Alternatively one may be dealing with the slow displacement of a catalyst poison,—water vapor, for example. In any case, there is certainly no evidence that aldehyde plays a primary rôle in the overall reaction, whatever may be the case in methane or ethane oxidation.

#### REACTION PERIOD

As already mentioned, these experiments were originally undertaken to obtain further information about the kinetics of propane oxidation subsequent to the induction period. Previous experiments (4, 8, 6) had emphasized the "all-or-nothing" character of the reaction (due to the disparity between the lengths of the induction and reaction periods); and had stressed the formation of methanol and formaldehyde with excess of propane, the induced dissociation of the hydrocarbon at higher temperatures, and the unimportance of "active" oxygen in view of the disappearance of peroxides when the reaction bulb was treated with potassium chloride.

As to the latter, it had been indicated that the presence of the salt did not materially decrease the overall reaction rate, as had been the case in the methane-oxygen and hydrogen-oxygen reactions (7, 5). In view of the elimination of peroxide by this treatment and the repressive influence of packing, it appeared that some effect should be observed. This point was therefore especially investigated. Some suppression by coating does in fact occur, as will later appear.

#### EXPERIMENTS BEFORE COATING

The first experiments were conducted with a clean Pyrex bulb 2.5 cm. in diameter and 18 cm. long. This was rinsed with nitric acid and water before being sealed in place. The bulb was heated electrically, temperature being controlled manually within  $1^{\circ}\text{C}.$ , and read on a mercury thermometer graduated in half-degrees. The propane and oxygen (tank gases) were measured into a mixing bulb, and thence passed to the reaction tube. The acetaldehyde was vaporized into the evacuated reaction bulb up to the desired pressure before the reactants were run in. The reaction bulb was adequately but not exhaustively evacuated after each run by means of a Langmuir pump connected to a liquid air trap and Hyvac pump. The exit tube from the reaction bulb was heated by a resistance winding to prevent condensation.

As already mentioned, with 300 mm. of each gas at  $280^{\circ}\text{C}.$  (no acetaldehyde) there was a 40-min. induction period followed by a 5-min. reaction period.

A preliminary attempt was made to cut the induction period by addition of 10 mm. of ethylene oxide to the reactants (300 mm. of each). This was ineffective. The pressure rose 5 mm. in the first 29 min., after which a further rise of 102 mm. completed the reaction in 5 min. more. In another run, 25 mm. of ethylene oxide was allowed to remain in the reaction bulb 23 min., after which the reactants were added. This was somewhat more effective. The pressure rose 4 mm. in 11 min., after which a rise of 101 mm. completed the reaction in another 5 min.

Since the induction period was more effectively eliminated with acetaldehyde, this was used in all subsequent runs.

A series of experiments with 5 mm. of acetaldehyde as "primer" was carried out at  $270^{\circ}\text{C}.$  Results appear in table 1.

There is an experiment with approximately 200 mm. of each gas; the same with 200 mm. of nitrogen added; an experiment with 200 mm. of propane and 400 mm. of oxygen; and one with 400 mm. of propane and 200 mm. of oxygen. The parallelism among the first three with the same initial propane concentration is obvious. All three accelerate to nearly the same degree up to about 60 mm. pressure increase, at which point all

the oxygen in the first two is consumed. (On the basis of previous work two volumes of oxygen react with one of propane.) Evidently neither excess of oxygen nor the presence of nitrogen affects this acceleration. This indicates that the rate is really independent of oxygen concentration, and that diffusion to the walls is not a factor. The rate is, however, strongly dependent on the propane concentration.

TABLE 1  
*Reaction at 270°C. (5 mm. of acetaldehyde)*  
Uncoated bulb

	INITIAL PRESSURE IN MILLIMETERS			
	202	211	205	407
C <sub>3</sub> H <sub>8</sub> .....	199	197	384	203
O <sub>2</sub> .....		202		
N <sub>2</sub> .....				
Time	Pressure rise			
min.	mm.	mm.	mm.	mm.
1	0	0	0	1
2	0	0	0	2
3	1	1	1	6
4	2	3	2	14
5	4	5	3	28
6	7	9	6	57
7	12	15	10	63
8	19	22	17	64
9	27	30	26	
10	36	41	34	
11	45	51	45	
12	55	59	55	
13	60	60	63	
14	61		72	
15			79	
20			103	
25			118	
30			119	

#### EXPERIMENTS AFTER COATING WITH POTASSIUM CHLORIDE

Following the experiments just described, the reaction bulb was dismounted and filled with dilute potassium chloride solution. After standing several days, it was thoroughly drained and then slowly dried with gentle heating and suction. There was no visible coating on the bulb, but subsequent experiments showed a marked change in activity. The induction period (300 mm. of each gas at 280°C. with no acetaldehyde) rose from 40 min. to over five hours. Addition of acetaldehyde shortened the induction period, but the subsequent reaction was still slower than before coating, as shown in table 2.

TABLE 2  
*Comparison of runs before and after coating*  
Temperature, 270°C.; 5 mm. of acetaldehyde added

INITIAL PRESSURE IN MILLIMETERS		TIME IN MINUTES*	
C <sub>2</sub> H <sub>2</sub>	O <sub>2</sub>	Before	After
400	200	1	3
200	400	2	22

\* This is the time required for the pressure to rise from 20 to 40 mm. above the initial value.

TABLE 3  
*Reaction at 280°C. (10 mm. of acetaldehyde) after coating with potassium chloride*

C <sub>2</sub> H <sub>2</sub> ..... O <sub>2</sub> ..... N <sub>2</sub> .....	INITIAL PRESSURE IN MILLIMETERS				
	195 196	215 198 204	213 406	408 204	295* 289
Time	Pressure rise				
min.	mm.	mm.	mm.	mm.	mm.
1	0	1	0	1	0
2	0	4	1	4	0
3	1	5	1	12	1
4	2	6	1	26	1
5	2	8	1	49	1
6	3	10	1	56	2
7	3	13	1	57	2
8	3	15	1		3
9	4	18	2		4
10	4	22	2		5
11	5	26	2		7
12	5	30	3		10
13	5	35	3		14
14	6	40	3		19
15	6	45	4		26
16	7	50	4		36
17	7	55	4		48
18	7	59	5		63
19	8	60	5		77
20	8	60	6		87
30	14		10		87
40	20		17		
50	27		34		
60	38		63		
70	49		90		
80	56		103		
90	57		112		

\* In this run with approximately 300 mm. of each gas, only 5 mm. of acetaldehyde was added.

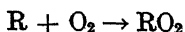


A set of experiments corresponding to those made before coating was carried out. In order to keep the induction and reaction periods within reasonable bounds, the temperature was raised from 270° to 280°C. and it was found advisable to use 10 mm. of acetaldehyde as "primer." Results appear in table 3.

It is evident that the coating of potassium chloride has completely changed the relationships. Addition of nitrogen now very materially increases the rate, as does an excess of oxygen, once the long induction period has terminated. This rather clearly indicates the importance of diffusion in the coated bulb. The same no doubt applies in part to the marked increase in rate produced by excess of propane.

#### DISCUSSION

These results have materially altered the writer's conclusions about the nature of the slow oxidation of the higher paraffins. It appears that the destructive action of potassium chloride-treated walls on peroxides is more important than previously concluded (4, 8, 6). The flow experiments at 300–400°C. and 1 atm. had indicated that there was no accompanying change in rate. It is now evident that the rate does decrease rather markedly under conditions favoring destruction of peroxides at the treated wall. One may therefore conclude that peroxides do in fact play an essential rôle in the case of the higher paraffins, whatever may be the fact for methane and ethane. It is to be emphasized that the peroxides in question are not of the peracid type, as shown by the analytical evidence (4, 8, 6) and by the relative ineffectiveness of acetaldehyde as a "primer." Beyond this their nature cannot at present be specified. The writer naturally is inclined to believe that the reaction.



is involved, as suggested by von Elbe and Lewis (9). This was previously avoided because of the supposed unimportance of peroxides. However, if one may argue from the slow but persistent increase in rate, sometimes nearly to the very end of reaction, a more stable intermediate would seem to be required. Possibly the transient compound  $RO_2$  is stabilized by formaldehyde (which is present) to give an hydroxi-peroxide, also suggested by von Elbe and Lewis. For the rest the scheme of the latter authors seems fairly well to exhaust the possibilities.

#### SUMMARY

In the slow oxidation of propane at 270–280°C. it has been found that treating the Pyrex reaction bulb with potassium chloride greatly lengthens the induction period, thus indicating that the preliminary reaction occurs

on the surface. Addition of small amounts of acetaldehyde shortens but does not eliminate the induction period, a fact which confirms previous conclusions that peracids (formed from aldehyde) are unimportant in the reaction scheme. Experiments after the potassium chloride treatment show that conditions favoring access to the walls diminish the rate of reaction markedly. This, together with the previously observed destructive action of the treated wall on peroxides, indicates that the latter play an essential rôle in the slow oxidation of the higher paraffins, whatever may be the case for methane and ethane.

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DISCUSSION<sup>1, 2</sup>

BERNARD LEWIS AND GUENTHER VON ELBE: Dr. Pease has brought out some rather striking new facts. At 270°C. in an uncoated vessel the reaction rate of propane oxidation was found to be very little accelerated by the addition of nitrogen. After coating the wall with potassium chloride the reaction rate dropped sharply, and in order not to make the experiments unduly tedious the temperature had to be raised to 280°C. and a larger amount of acetaldehyde added. Now the rate proved to be strongly accelerated by nitrogen. The substitution of nitrogen by oxygen showed no comparable effect. It is possible to advance an explanation consistent with a branched-chain mechanism such as has been proposed by the writers (J. Am. Chem. Soc. **59**, 976 (1937)) in conjunction with the diffusion theory of chain reactions (von Elbe and Lewis: J. Am. Chem. Soc. **59**, 970 (1937)) for the case of chain breaking at the wall.

For low chain-breaking efficiency of the wall, the diffusion theory demands that the reaction be independent of the presence of inert gas. For high chain-breaking efficiency, such as may be supposed to exist in potassium chloride-coated vessels, the reaction rate will be much smaller and it will be accelerated by inert gas.

The fact that oxygen does not produce an effect comparable to that of

<sup>1</sup> Published by permission of the Director, U. S. Bureau of Mines, and the Director, Coal Research Laboratory, Carnegie Institute of Technology.

<sup>2</sup> Received September 25, 1937.

nitrogen suggests that it should not be regarded only as an inert gas. It may be possible to connect this effect with the inhibition by oxygen of the methyl alcohol-forming chain reaction discovered by Pease (J. Am. Chem. Soc. **57**, 2296 (1935)). We proposed this inhibition (J. Am. Chem. Soc. **59**, 976 (1937)) to consist of the oxidation of the chain carrier  $\text{CH}_3\text{O}$  to  $\text{CO}$ ,  $\text{H}_2\text{O}$ , and  $\text{OH}$ . There are now two principal chain carriers, namely,  $\text{CH}_3\text{O}$  and  $\text{OH}$ , the former being predominant at high percentages of hydrocarbon and the latter at high percentages of oxygen. It is possible that  $\text{CH}_3\text{O}$  is a more efficient promoter of the reaction than  $\text{OH}$ , either because it is destroyed at the wall at a smaller rate or because of its greater reactivity in the gas phase, or both.

We have expressed the view that the wall plays the dual rôle of initiating and destroying chains, the chain-initiating reaction to consist of the dissociation of peracids formed heterogeneously from aldehydes. Such a view would appear to be consistent with experimental facts concerning aldehyde oxidation brought out by Pease and others. It would imply that potassium chloride not only increases the chain-breaking efficiency of the wall but also decreases the rate of chain initiation by the destruction of peracids. The peracids formed in the chain-initiating process are of necessity short-lived at the high temperatures in question, as is also shown by the analytical results in studies of the high-temperature oxidation of aldehydes; in any case they would be present in very small concentrations.

## OBSERVATIONS ON THE OXIDATION OF PROPANE

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As a result of an investigation carried out on the effect of antiknocks on the combustion of hydrocarbons, Egerton and Gates (2) concluded that a product of the oxidation of the aldehydes formed in the oxidation of the hydrocarbon assisted the autoxidation of the aldehyde stage of the combustion as well as the initial stage. The effect of inhibitors in delaying the combustion and Semenoff's work (7) on the oxidation of phosphorus led to the view that the combustion of hydrocarbons took place by a chain reaction mechanism (1). A study of the oxidation of pentane (6) helped to confirm this view.

Many investigations have been carried out in order to elucidate the nature of the mechanism of hydrocarbon combustion, but precise knowledge is still lacking. The observations on the oxidation of propane which follow, though they do not purport to do more than indicate some features of the combustion, add a few further facts to those already gathered, particularly by Pease in his studies of the oxidation of this hydrocarbon (5).

There is a general similarity in the combustion behavior of the straight-chain paraffin hydrocarbons and even of the olefins, which makes it probable that the propagation of the chain is effected in a similar way for different hydrocarbons, excepting that the mechanism in the higher ignition ranges is different in certain respects from that in the lower ranges.

Experiments have been made by the flow method and by the usual "static" method in which the gas mixture is maintained in a vessel at constant temperature. The surface conditions were varied, and small quantities of compounds which may be intermediates in the reactions were added in some of the experiments. The results are in general agreement with those obtained by Pease, but the analyses indicate that hydrogen peroxide is formed, as well as probably a small quantity of acetyl peroxide. Dihydroxymethyl peroxide is present in the condensate formed from formaldehyde and hydrogen peroxide. The amount of peroxide found depends on the surfaces to which the vapor is exposed.

## FLOW SYSTEM

A measured volume of gas (usually 600 cc.) was drawn at a constant rate through a reaction vessel (10 cm. long and 1.1 cm. in diameter) maintained at a constant temperature. A tube projected into a trap cooled to  $-40^{\circ}\text{C}$ . at the exit end of the reaction vessel. The gas then passed through a water scrubber into an aspirator; a second tube containing 2,4-dinitrophenylhydrazine sulfate could be used to test whether the absorption of the aldehyde was complete. The volume of gas and weight of condensate were ascertained.

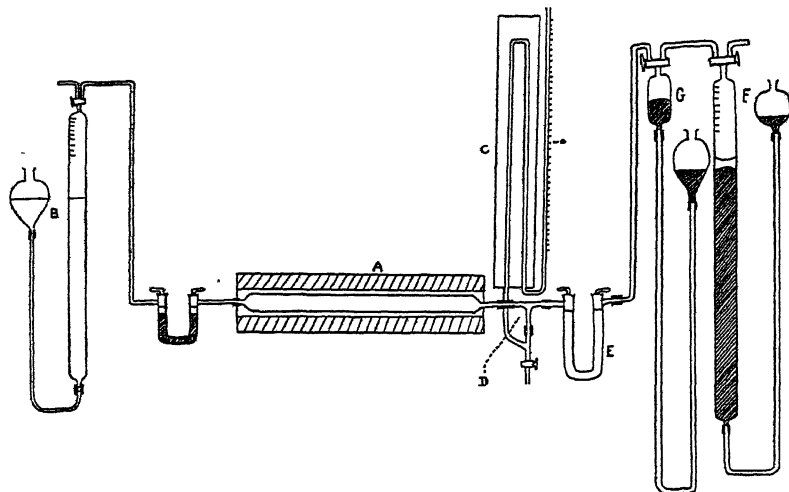


Fig. 1. Static system

## STATIC SYSTEM

The silica reaction vessel (A) (42 cm. long x 1.4 cm. in diameter) was connected at one end to a gas buret (B) and at the other to a manometer (C) and T-tube (D). The vessel could be connected either to a Hyvac pump or to a trap (E) for condensation of the liquid products, the gas being sucked into a second gas buret (F) by a Toepler pump arrangement (G). In order to obtain sufficient condensate six separate charges of gas were allowed to react to as nearly as possible the same extent as measured by the pressure change. Any aldehyde escaping the trap was collected in a small quantity of water in the gas buret (F). (See figure 1.)

Analyses were made, for peroxide by the iodine method using ammonium molybdate as catalyst, for total aldehydes by titrating the alkaline solution before and after oxidation with hydrogen peroxide solution, and for

formaldehyde by the mercuric chloride method after distillation to remove alcohols. Ethyl and methyl alcohols were determined in this distillate by oxidation by dichromate (8). The amount of higher alcohol was found to be small, so that little error was introduced if it was all assumed to be ethyl alcohol. The gas analysis was carried out in a Bone-Newitt apparatus with the addition of a tube of palladinized asbestos for the hydrogen determination.

#### STATIC METHOD RESULTS

The results shown in table 1 were obtained using a clean silica vessel washed with hydrofluoric acid, and the same vessel after washing with saturated solutions of potassium chloride and of sodium chloride, respectively.

TABLE 1  
*Results obtained by static method*  
For 1:1 mixture at 1 atm. initial pressure

VESSEL	TEMPERATURE IN °C.	USED		PRODUCTS IN GRAM-MOLES $\times 10^{-4}$									
		C <sub>2</sub> H <sub>6</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO	C <sub>2</sub> H <sub>4</sub>	H <sub>2</sub>	CH <sub>4</sub>	HCHO	RCHO	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	H <sub>2</sub> O
Silica (washed).....	322	25	47.4	5.3	28.2	2.8	0.8	6.9	3.7	2.0	8.0	0	41
Silica (KCl).....	351	21.8	43.9	5.5	23	4	0.74	2.6	3.4	6.4	0	40.5	
Silica (KCl).....	337	22.8	46	7.8	25.2	4.6	0.6	4.4	2.8	3.2	6.7	0	39
Silica (NaCl).....	323-338	24.8	45.7	7.7	19.6	3.6	1.4	6.4	4.1	0.7	3.6	1.8	46
Silica (NaCl).....	351	23.1	42.3	6.0	22.6	5.3	0.3	3.4	2.8	2.2	4.1	1.6	39
Silica (NaCl).....	351	23.1	42.5	5.7	21.4	4.6	0.9	4.9	2.5	2.9	3.1	0.8	41
Silica (Fe <sub>2</sub> O <sub>3</sub> ).....	355	12.4	28.4	8.9	10.7	1.3	0.3	4.0	0	2.3	0	0	25
Graphite tube.....	320	6.7	20.5	11.5	5.2	0.6	1.0	3.9	0	2.5	1.6	0	9

tively. The reactions were allowed to go to completion. It was found that the induction period in successive experiments in the coated tubes became less, reaching a minimum, indicating that products which can initiate reaction are absorbed from the products of the previous run.

The temperature made no appreciable difference in the final composition of the products; it affected, however, the start and the time of the reaction, a higher temperature being needed to start the reaction in the case of the alkali-treated surfaces. The slower reactions were associated with a slightly higher amount of carbon dioxide, due probably to surface oxidation of aldehyde. There is throughout a close correspondence between the amount of oxygen used and the water formed.

The total aldehydes and alcohols were present in about the same amounts, along with nearly as much unsaturateds which were proved to contain both propylene and ethylene.

## FLOW EXPERIMENTS

The yields of products obtained are similar to those of the static experiments, provided the reaction is completed in the time of passage-through the tube. The variation in contact time once the induction and reaction period has been exceeded has very little effect.

The peroxides, noted by Pease in the flow experiments, are not obtained in the static experiments, but they are obtained by the flow method using a clean acid-washed silica tube. The yield of peroxide is very susceptible to "poison"; it falls off after a few experiments but the surface can be cleaned again by acid wash. No peroxide is formed if soda glass reaction tubes are used, though Pyrex glass, as used by Pease, was found to behave similarly to quartz. If the hot gaseous products of reaction are led through a soft glass tube, the peroxides are immediately destroyed; so in the

TABLE 2

PRODUCTS	EXPERIMENT 1	EXPERIMENT 2	
	Residue at 40°C.	Distillate, $\frac{1}{3}$ of the volume	Residue, $\frac{2}{3}$ of the volume at 54°C.
CH <sub>3</sub> OH.....	Trace	0.300	Trace
HCHO.....	0.309	0.016	0.045
CH <sub>3</sub> CHO.....	?	0.076	0.085
Oxygen for acid ....	?	0.000	0.037
Peroxide as H <sub>2</sub> O <sub>2</sub> .....	0.180	0.004	0.022
Total.....	0.489	0.396	0.193
H <sub>2</sub> O.....	0.511	0.604	0.807

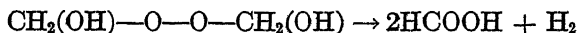
static experiments no peroxides were found, though they can be found if the whole reaction vessel is plunged into cold water before removal of the products. These results show that peroxides can be formed, but can only remain in the products if the surfaces to which the gases are exposed do not destroy them.

The peroxide-containing condensate from a prolonged flow experiment was fractionally distilled *in vacuo* at 2.2 cm. pressure. The distillate proved to be mainly aqueous methyl alcohol. Decomposition of the peroxides occurred during distillation; in experiment No. 1 the amount of peroxide estimated as hydrogen peroxide was approximately 10 per cent of the total liquid before distillation. On rapid distillation violent explosion occurred.

Table 2 gives the analysis per gram of the products. The quantity of formaldehyde and aldehydes includes the corresponding acids which may be present, though no acid was found in the distillate; the amounts

were determined by oxidation of the aldehydes after titration for acid, the oxygen equivalent to the acid being thus obtained. Peroxides are present other than peroxides which give rise to acid on decomposition. The acidity is appreciable only when large amounts of peroxide are formed and is not equivalent to the total peroxide.

The dihydroxyperoxide  $(\text{OH})\text{CH}_2\text{—O—O—CH}_2(\text{OH})$ , obtained by Lenher (4) during the oxidation of ethylene, is no doubt present. The ratio of formaldehyde to hydrogen peroxide in the residue in experiment No. 1 above is 0.0103 gram-mole/0.0053 gram-mole or 2/1. The behavior with potassium iodide is suggestive of this compound, but also alkaline decomposition of the peroxide condensate yielded a gas containing 80 per cent hydrogen and 20 per cent oxygen, the hydrogen being formed according to the reaction



This peroxide, which is appreciably dissociated at room temperature, is formed from formaldehyde and hydrogen peroxide and probably does not exist in the uncondensed state. This is borne out by the observation that the hydrogen content of the vapors containing peroxide from the flow experiments is not increased by passage through a soda glass tube. The evidence points to hydrogen peroxide and acetyl peroxide being formed, both of which can decompose in the vapor state to give products which are not acid, though the latter may under certain circumstances give rise to acetic acid. There is no evidence for the formation of alkyl peroxides which on decomposition would give rise to further aldehyde or alcohol, unless in too small a quantity to be detected, but their transitory formation and decomposition is possible. (It is noteworthy, however, that in experiments in which ethyl hydrogen peroxide and acetyl peroxide were injected into an engine cylinder, they were collected again from a sample valve with less decomposition than in the case of hydrogen peroxide.)

The fact that no peroxide is formed from coated tubes is no evidence that peroxide-forming radicals are not present during the reaction; it merely means that the surface destroys such peroxide as is formed. The fact that there is little difference in the aldehydes formed in the coated tubes as compared with uncoated tubes indicates that hydrogen peroxide is the main peroxide existing in the vapor, but this is contrary to Pease's conclusion.

The figures for silica coated with iron oxide show an abnormal amount of carbon dioxide and no alcohols or formaldehyde. Experiments carried out in iron vessels will not be likely to give results similar to those found in glass or silica vessels, surface reaction of the products being enhanced. A graphite tube was also used with somewhat similar results.



Table 3 gives the amount of the various constituents of 1 g. of liquid condensate from flow and static experiments. The results indicate that except for a small variable amount of acids, the presence or not of peroxide makes little difference in the amounts of other products formed.

In the study of the effect of surfaces on the reaction, flow experiments are subject to the difficulty that if the induction period is long no appreciable reaction occurs, whereas if the flow is decreased or the temperature raised sufficiently to start the reaction, the reaction is quickly completed and it is not easy to get reliable analyses of the products before the com-

TABLE 3  
*Constituents of 1 g. of liquid condensate from flow and static experiments*

CONSTITUENTS IN GRAM-MOLES $\times 10^{-4}$						PER CENT H <sub>2</sub> IN GAS	CONDITIONS	TEM- PERA- TURE IN °C.
Peroxide cal- culated as H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O by difference	CH <sub>3</sub> OH C <sub>2</sub> H <sub>5</sub> OH	HCHO HCOOH	CH <sub>3</sub> CHO CH <sub>3</sub> COOH	HCOOH CH <sub>3</sub> COOH			
22.7	300	54.6	38.4	19.4	6.2	1.5	Flow system	
27.5	349	40.4	33	21.4	9.8	2.3	Silica	335
17.5	(385)	26.3	31.5	23.4	8.2	1.6		
	375	44	30.7	19.2	0	1.7	Static system	328
	331	64.6	29.9	23.0	(1.3)	1.0	Silica	322
0.2	337	63.4	30.7	31.4	0.7	0.8	Flow system	
	346	62.2	35	17.9	1.5	0.9	KCl on silica	344
	343	51	33.6	27	0	1.2	KCl on glass	358
	332	57.0	23.8	31.0	3.8	0.8	Static system	337
	346	54.6	21.2	29.1	1.7	1.0	KCl on silica	351
	352	52.4	25.7	20.2	3.7	1.8	Static system NaCl on silica	351

pletion of the reaction. The difficulty is greater because, when once started, the presence of reaction products tends to diminish the induction period.

In static experiments, on the other hand, although they provide means of obtaining analysis of the products at different stages of the reaction, the state of the surface is not the same throughout because of the changing composition of the gases.

Table 4 shows some analyses of products removed at predetermined pressures in a static experiment (silica bulb) with a 1:1 mixture at 1 atm. initial pressure: (a) The ratio for this 1:1 mixture of the gases O<sub>2</sub> and C<sub>3</sub>H<sub>8</sub>

used is approximately 2:1, as found by Pease. (b) The carbon monoxide, carbon dioxide, and methyl alcohol increase throughout, being formed as the result of decomposition of products formed by chain reactions. (c) The water, hydrogen, and aldehydes increase linearly with the amount of reaction, being products probably of chain reactions (their percentage remains constant except in the first stages). (d) The propylene and

TABLE 4

*Analyses of products removed at predetermined pressures in a static experiment*

GAS USED		PRODUCTS IN GRAM-MOLES $\times 10^{-4}$ PER $10^{-3}$ GRAM-MOLES OF $C_3H_8$ USED										TEMPERATURE IN $^{\circ}C$ .
$C_3H_8$	$O_2$	$O_2$ (used)	$CO_2$	$CO$	$C_2H_6$	$H_2$	$CH_4$	$HCHO$	$RCHO$	$CH_3OH$	$H_2O$	
8.1	13.3	16.4	1.0	5.3	2.7	0.6	5.7	0.7	1.0	0.8	17.9	320
14.2	24.0	16.9	1.55	8.4	1.76	0.3	5.3	1.4	1.1	2.4	17.4	325
22.4	39.8	17.8	1.34	9.4	1.83	0.3	1.1	0.9	1.2	2.0	17.4	340
25.0	47.4	18.9	2.1	11.3	1.1	0.3	2.7	1.5	0.8	3.2	16.8	322
25.7*	50.2	19.5	2.3	9.7	0.7	0.3	2.6	1.2	0.6	2.7	18.2	307

\* Trace of acetaldehyde added to shorten induction period.

TABLE 5

*Effect of composition of the initial mixture at 1 atm. initial pressure on the composition of the products*

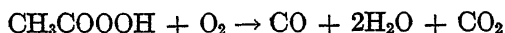
INITIAL MIXTURE $C_3H_8:O_2$	PRODUCTS IN GRAM-MOLES $\times 10^{-4}$ PER $10^{-3}$ GRAM-MOLES OF $C_3H_8$ USED										TEMPERATURE IN $^{\circ}C$ .
	$O_2$ (used)	$CO_2$	$CO$	$C_2H_6$	$H_2$	$CH_4$	$HCHO$	$CH_3CHO$	$CH_3OH$	$H_2O$	
1:1	18.9	2.1	11.3	1.1	0.3	2.76	1.48	0.80	3.2	16.8	323
	17.8	1.34	9.4	1.83	0.3	1.12	0.9	1.16	2.0	17.4	340
	18.7	1.9	10.6	1.1	0.2	2.0	1.5	0.95	2.1	18.5	326
2:1	11.4	0.7	6.3	1.74	0.3	3.6	1.1	1.35	1.70	11.1	340
	12.8	1.25	6.8	2.0	0.3	3.0	2.17	0.96	2.66	10.6	340
4:1	10.7	0.68	5.3	2.38	0.7	2.8	1.81	0.96	1.81	10.2	331

methane appear to be formed early in the reaction. (e) The ratio of water formed to oxygen used is 1:1.

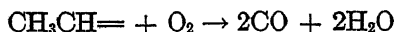
The experiments recorded in table 5 show the effect of the composition of the initial mixture at 1 atm. initial pressure on the composition of the products: (a) The ratio of water formed to oxygen used remains at about 1:1. (b) The ratio of oxygen to propane used, however, changes from 2:1 for the 1:1 initial mixture to 1:1 for the 4:1 initial mixture, the difference between the 1:1 and the 2:1 mixtures being much greater than

for the 2:1 and 4:1 mixtures. (c) The main difference between the 1:1 and the 2:1 mixtures is in the carbon monoxide and water formed.

These results indicate that the oxygen in the 1:1 mixture, owing to its higher concentration, provides an intermediate product which directly forms carbon monoxide and water, and about 6 moles more oxygen are consumed per 10 moles of propane reacting than for the 2:1 mixture (four oxygen atoms to carbon monoxide, seven to water, and about two to carbon dioxide). The excess of oxygen in the latter case and in the 4:1 mixture is insufficient to permit appreciable further reaction to carbon monoxide and water. It may be that reactions such as



and



break the chains or destroy products, thus accounting for the fact that a large excess of oxygen tends to inhibit the slow reaction.

TABLE 6

$\text{C}_3\text{H}_8$ USED	$\text{O}_2$ USED	PERCENTAGE PRESSURE INCREASE	PERCENTAGE INCREASE IN $\text{C}_3\text{H}_8$ USED	PERCENTAGE INCREASE IN $\text{O}_2$ USED
8.1	13.3	4.5	0.56	0.34
14.2	24	7.9	0.56	0.34
22.7	41.1	17.3	0.76	0.42
22.4	39.8	17.2	0.77	0.42
25	47.4	19.8	0.79	0.42
26.3	49.2	21.45	0.82	0.43

In the initial stages of the oxidation, the increase in the number of molecules caused by the reaction of one propane molecule is less than in the later stages, probably owing to dissociation of reaction products; pressure-time curves would need therefore to be corrected before direct deductions about the kinetics of the reaction could be made from them (see table 6).

The effect of the addition of certain individual reaction products to the initial 1:1 mixture at 300–340°C. was as follows: formaldehyde increased the induction period; acetaldehyde greatly decreased the induction period and increased the yield of methyl alcohol; propylene decreased the induction period; methyl alcohol had no effect.

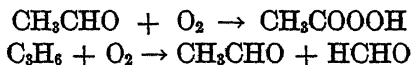
These and other experiments which are being made at high and low

pressures by a variety of methods are part of an extensive investigation of hydrocarbon combustion which is being carried out in the Department of Chemical Technology at South Kensington. Until some of this other experimental work is more advanced, it is not proposed to discuss the above results in detail.

Several schemes to describe the behavior of hydrocarbons on oxidation have been suggested recently: e.g., Norrish's oxygen atom chain, Pease's "methoxyl radical" chain, the "peroxide radical" chain elaborated by Ubbelohde, and a combination and extension of these presented still more recently by Lewis and von Elbe. It is not intended to elaborate any further schemes; a true interpretation will probably be found within the range of suggestions which have been put forward, but the experimental facts must be established before a satisfactory theory can be developed. The knocking characteristics of hydrocarbons early convinced one of the authors (3) that organic peroxides were playing a part in the oxidation of hydrocarbons. Particularly does that seem to be so now that those characteristics are linked by the work of Townend and his collaborators with the pressure ignition characteristics, but experimental elucidation of their exact function is still lacking. Experimental data are still needed to decide exactly what occurs under different conditions. It must also be pointed out that what happens in one part of the mixture undergoing reaction may be very different from the average behavior of the mixture, so that deductions from kinetics may be sometimes misleading; an exaggerated illustration of this is to be found in the pulsation phenomena of cool flames.

The oxidation of propane is characterized by (a) initiation by aldehyde, (b) early appearance of unsaturateds (propylene and ethylene), (c) formation of methyl alcohol and total aldehydes in approximately equivalent amounts, (d) destruction of peroxides at surfaces with apparently little change in the composition of the final products, and (e) formation of water approximately equivalent to the oxygen used.

A certain concentration of aldehyde or aldehyde peroxide is needed before reaction starts. It is possible that during this period the following reactions may take place:



As both the formation and oxidation of the propylene depend on the oxygen concentration, the final amount obtained is approximately the same, unless the time during which the propylene is exposed to oxidation is exceptionally long, as table 7 shows.

When propylene is added to a 1:1 mixture of propane and oxygen,

the final concentration of unsaturates obtained is approximately constant, as shown in table 8. The fact therefore that the concentration of propylene is greater at an early stage of the reaction and is not dependent on the propane concentration seems to indicate that its formation is associated with the products which initiate the reaction rather than with a direct process of dissociation of the propane. The total aldehydes formed in the reaction are approximately the same in amount as the methyl alcohol, when the oxygen concentration is low so that further oxidation is avoided. This indicates that both methyl alcohol and aldehyde are formed, probably

TABLE 7  
*Effect of oxygen concentration on the final amount of propylene*

INITIAL RATIO OF PROPANE TO OXYGEN	UNSATURATEDS IN GRAM- MOLES $\times 10^{-4}$	SURFACE CONDITION
4:1	4.2	Silica
2:1	4.4	Silica
2:1	4.8	Silica
1:1	4.1	Silica
1:1	4.3	Silica
1:1	4.6	NaCl coated
1:1	4.0	KCl coated
1:1	3.6	NaCl coated
1:1	4.6	KCl coated

TABLE 8  
*Effect of addition of propylene upon final concentration of unsaturates*

PROPYLENE ADDED IN GRAM-MOLES $\times 10^{-4}$	UNSATURATEDS IN FINAL GAS IN GRAM-MOLES $\times 10^{-4}$
0	4.4
3.6	3.9
7.6	4.3

as the products of a reaction chain. On further oxidation the acetaldehyde is burnt preferentially to formaldehyde, giving rise to cool flames; at higher temperatures the acetaldehyde probably dissociates to methane and carbon monoxide. At high pressures other alcohols are known to be formed, and it is probable that other reaction mechanisms come into play.

#### SUMMARY

1. Analyses of the products of the slow combustion of propane in oxygen by flow and static methods have been made.
2. Peroxides are found only when the surface does not destroy them too

fast to prevent their detection. In the vapor state hydrogen peroxide appears to be mainly present and dihydroxymethyl peroxide in the condensate.

3. Propylene is formed early in the reaction, possibly from the aldehydes which initiate the reaction.

4. Methyl alcohol and aldehydes appear to be formed by the same chain process.

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# THE OXIDATION OF HYDROCARBONS AT HIGH PRESSURE

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It is the purpose of this paper to give an account of the effect of pressure upon the formation and survival of oxygenated products during the slow (isothermal) combustion of hydrocarbons in air or oxygen at high pressures, and also to consider briefly the bearing of the results upon the theory of hydrocarbon combustion generally. The data available are unfortunately by no means as comprehensive as could be desired, but sufficient work has been done to leave no doubt but that pressure plays an important part in changing or modifying the course of oxidation during both slow and explosive combustion.

## THE RÔLE OF PRESSURE

It will be of interest to consider first the possible ways in which pressure may influence the course of a gaseous reaction. One of the direct consequences of raising the pressure is to increase proportionately the frequency of molecular collision; in so far as reaction velocity depends upon collision rate, it will undergo a corresponding increase with pressure. It is, therefore, frequently possible, by suitably increasing the pressure, to carry out a reaction at a temperature considerably lower than would be practicable under atmospheric conditions and by so doing to favor the survival of intermediate products which at higher temperatures would undergo rapid further oxidation or thermal decomposition.

Pressure may also modify the course of a reaction proceeding by a chain mechanism by deactivating the carriers and thus interrupting the chain. Furthermore, a sufficiently high pressure may, by forcing the molecules into close contact, produce such an alteration in their electrostatic fields as to give rise to induced or increased polarity. Lastly, pressure will influence a reversible reaction in accordance with the Le Chatelier principle of mobile equilibrium in the direction resulting in a diminution of specific volume or molecular density. Examples of all these effects are found in combustion reactions although, owing to their complex character, it is not always possible to account for the results on a quantitative basis.



## APPARATUS AND EXPERIMENTAL METHODS

In carrying out pressure oxidations in a small scale plant it is usually not practicable to make provision for adequate heat exchange, and in order to ensure substantially isothermal conditions the reacting medium must be diluted with a large excess of the combustible or with an inert gas or vapor such as nitrogen or steam; even in a large scale plant it is found advantageous to work with weak mixtures containing not more than 10 to 15 per cent of oxygen.

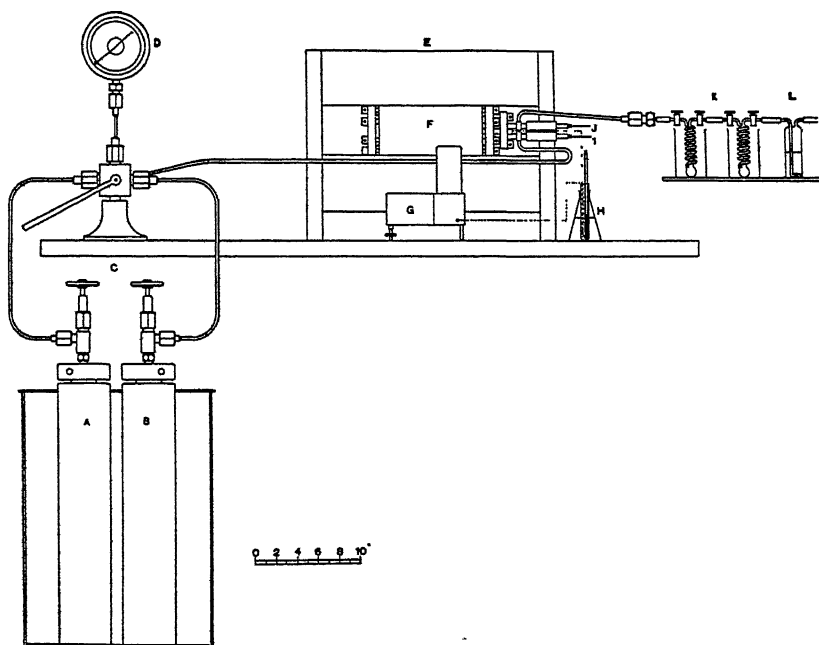


FIG. 1. Apparatus for the static method

Two methods have been generally employed: namely, (1) a static method in which a known quantity of the reactants is admitted into a heated reaction vessel and the progress of the reaction followed by the changes in pressure or composition of the medium, and (2) a flow method in which the reactants are passed at a measured velocity through a heated reaction vessel and the products are collected and analyzed.

Figure 1 shows diagrammatically an apparatus suitable for static experiments at pressures up to several hundred atmospheres. The previously mixed hydrocarbon and air or oxygen are compressed into the two steel cylinders A and B to a pressure considerably above the proposed working value, and in the case of the higher hydrocarbons the cylinders are main-

tained at a temperature sufficiently high to prevent any condensation taking place. The gases pass from the cylinders through the control valve C and the inlet valve I to the reaction vessel F, which is electrically heated. The inlet valve is closed, and after a time interval sufficient for the reaction to take place the contents of the vessel are released through the exit valve J and allowed to pass through a system of condensers K and absorber L, in which condensable and soluble products are removed, to a calibrated gas-holder. The initial pressure of the reacting medium is measured by the Bourdon gauge D and its temperature by a platinum-rhodium thermocouple situated in a steel tube traversing axially the reaction chamber.

For the flow method a more elaborate apparatus is required, one form of which is shown in figure 2. A and B are storage cylinders containing the reactants at a suitable high pressure. From the cylinders they pass

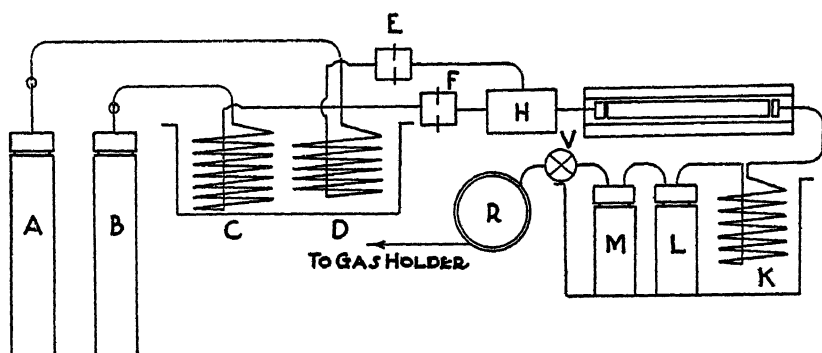


FIG. 2. Apparatus for the flow method

through separate pipe lines to the preheaters C and D and thence through orifice meters E and F to the premixing chamber H. From H they travel directly into the reaction chamber, which is electrically heated, and on emerging are rapidly cooled in the coil K; the condensable and soluble products are removed in the receivers L and M. The residual gases are then reduced to atmospheric pressure by the valve V and are passed through a meter R to a calibrated gas holder. Various adaptations and modifications of this apparatus can be used according to the nature of the investigation.

Of the two methods the static permits of more accurate control of experimental conditions, whilst the flow method enables larger amounts of material to be used and thus facilitates analyses of the complex mixtures of alcohols, aldehydes, and acids that are found in the products.

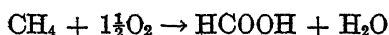
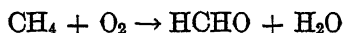
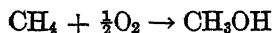
## OXIDATION OF METHANE

*General characteristics of the high-pressure reaction*

When a methane-oxygen mixture containing a large excess of the combustible or of an inert gas (e.g.,  $8\text{CH}_4 + \text{O}_2$ ) is maintained at a suitable temperature for slow reaction ultimately to take place there is an "induction" period which may last many minutes, during which little or no oxidation takes place, followed by a reaction period during which the whole of the free oxygen is consumed and various intermediates and end products are formed. The temperature at which reaction first becomes noticeable is found to depend *inter alia* upon mixture composition and pressure; thus an  $8\text{CH}_4 + \text{O}_2$  medium will react at comparable rates under the following conditions (5):

<i>Temperature in °C.</i>	<i>Pressure in atmospheres</i>
410	.1
360	48
340	105
337	150

The products of the combustion are methyl alcohol, formaldehyde, formic acid, the two oxides of carbon, and steam; hydrogen is found only in exceptional circumstances when the reaction is of an explosive character. The stoichiometric equations for the formation of these compounds, namely,



indicate that whilst formaldehyde is formed with no change in volume, both methyl alcohol and formic acid result in a contraction. The proportions in which they survive depend largely upon experimental conditions and in particular upon temperature and pressure. In a static system, for example, the yields recorded in table 1 were obtained for an  $8.1\text{CH}_4 + \text{O}_2$  medium at 106.4 atm. and various temperatures between 336° and 355°C.

The data in table 1 show clearly that at constant pressure there is an optimum temperature or rate of reaction for the survival of both alcohol and aldehyde, which is probably determined by their respective rates of formation and further oxidation. It is also noticeable that at the higher temperature, when reaction takes place rapidly with a comparatively large temperature rise, the yields of intermediates are considerably reduced, whilst the  $\text{CO}/\text{CO}_2$  ratio increases.

The effect of increasing the initial pressure is to increase progressively the quantities of alcohol surviving in the products, providing always that

TABLE 1

*Products from the slow combustion of an 8.1CH<sub>4</sub> + O<sub>2</sub> medium at 106.4 atm. (5)*

INITIAL TEMPERATURE	RISE IN TEMPERATURE	DURATION OF		PRODUCTS AS PER CENT OF METHANE BURNT		RATIO CO/CO <sub>2</sub> IN GASEOUS PRODUCTS
		Induction	Reaction	CH <sub>3</sub> OH	HCHO	
°C.	°C.	min.	min.			
336	4	53	35	10.1	0.30	0.05
339	10	14	22	14.1	0.36	0.01
341	14	2.5	9.5	22.3	0.75	1.5
343	10		12	20.0	0.93	1.0
347	17	2.5	5.5	16.6	0.30	
352	26*	1	1	9.8	0.95	3.9
355	37*	0†	1	3.8	Trace	4.2

\* Probable formation of flame during combustion.

† Comparable with time for filling reaction vessel.

TABLE 2

*The influence of pressure upon the survival of methyl alcohol and formaldehyde in the slow combustion of an 8.1CH<sub>4</sub> + O<sub>2</sub> medium (5)*

INITIAL PRESSURE	INITIAL TEMPERATURE	DURATION OF OXIDATION	PRODUCTS AS PER CENT OF METHANE BURNT		RATIO CO/CO <sub>2</sub>
			CH <sub>3</sub> OH	HCHO	
atm.	°C.	min.			
10	400	10	1.1	Trace	0.06
25	385	7	4.8	0.66	0.15
40*	372	15	6.1	1.20	0.05
48	373	4	13.7	0.80	0.35
106.4	341	12	22.3	0.75	
149*	341	16	19.0	0.60	0.08

\* Not quite optimum conditions.

TABLE 3

*The influence of diluents upon the yields of methyl alcohol and formaldehyde from the combustion of a 2CH<sub>4</sub> + O<sub>2</sub> medium at 50 atm. pressure (5)*

INITIAL MIXTURE 2CH <sub>4</sub> + O <sub>2</sub> +	TEMPERATURE	TIME OF REACTION	PRODUCTS SURVIVING, IN CC. AT N.T.P.	
			CH <sub>3</sub> OH	HCHO
	°C.	min.		
6.5N <sub>2</sub>	397	16	48	2.7
6.5H <sub>2</sub> O	400	2	43	1.6
6.5CO <sub>2</sub>	390	8	50	3.0
6.5CH <sub>4</sub>	397	1	80	4.6

the reaction temperatures are so adjusted as to give comparable conditions in respect of reaction velocities. Formaldehyde, which is only found in small quantities, shows little response to pressure (see table 2).

The oxidation proceeds in a similar way when air is substituted for oxygen or when the medium is diluted with nitrogen, carbon dioxide, or steam, but in all such cases the reaction is slowed up and the yields of alcohol are diminished (table 3).

#### OXIDATION OF ETHANE

Ethane oxidizes rather more readily than does methane, but in other respects the characteristics of its combustion are similar; in both cases the most reactive mixture is one containing the hydrocarbon and oxygen in the ratio 2:1. The products from its slow combustion at high pressures

TABLE 4

*Products from the reaction of an  $8C_2H_6 + O_2$  medium at 50 atm. and various temperatures*

INITIAL TEMPER- ATURE	DURATION OF		PERCENTAGE OF THE CARBON OF THE ETHANE BURNT SURVIVING AS										
	Induc- tion	Reac- tion	C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> OH	CH <sub>3</sub> CHO	HCHO	CH <sub>3</sub> COOH	HCOOH	CO	CO <sub>2</sub>	CH <sub>4</sub>	Total liquid products	Total gaseous products
°C.	min.	min.	14.8	10.8	4.7	0.2	15.2	0.3	19.3	32.5	Nil	46.0	51.8
279.2	18.0	100.0	14.8	10.8	4.7	0.2	15.2	0.3	19.3	32.5	Nil	46.0	51.8
286.0	7.0	3.8	24.4	14.1	8.3	2.0	1.7	0.9	34.8	10.0	Nil	51.4	44.8
288.0	6.5	3.8	20.5	11.3	7.3	1.2	2.3	0.7	31.6	7.1	13.7	43.2	52.4
289.0	4.2	2.8	16.0	14.4	4.9	2.0	2.4	0.4	36.0	4.6	20.7	40.1	61.3
294.0	2.0	3.2	17.2	14.1	5.2	1.9	Nil	0.7	40.8	7.8	8.1	39.1	56.1

are ethyl and methyl alcohols, acetaldehyde, formaldehyde, acetic and formic acids, the two oxides of carbon, methane, and steam (3). The proportion in which the carbon of the ethane burnt is distributed amongst these products depends upon the experimental conditions; thus, for example, in the case of an  $8C_2H_6 + O_2$  medium reacting on a static system at 50 atm. the relative yields are as shown in table 4.

The results indicate that in so far as ethyl alcohol and acetaldehyde are concerned a temperature giving a medium rate of reaction is most favorable to their survival; acetic acid on the other hand requires a very slow reaction rate, whilst methyl alcohol varies little throughout the series.

The effect of increasing the pressure is favorable to these products containing two carbon atoms but reduces the yields of methyl alcohol and formaldehyde (see table 5).

From the point of view of the mechanism of hydrocarbon combustion it

is important to know something of the order in which the various intermediates are formed and to distinguish between those participating in the main reaction and those resulting from secondary reactions. Some light is thrown on this matter by the results of experiments carried out by the flow method (9); if, for example, a hydrocarbon-oxygen mixture is passed through a heated zone at progressively increasing velocity, then, provided

TABLE 5

*The influence of initial pressure on the survival of intermediate products from the reaction of an  $8C_2H_6 + O_2$  medium*

INITIAL PRESSURE	INITIAL TEMPER- ATURE	DURATION OF REACTION	PERCENTAGE OF THE CARBON OF THE ETHANE BURNED SURVIVING AS						
			$C_2H_5OH$	$CH_3OH$	$CH_3CHO$	$HCHO$	$CH_3COOH$	$HCOOH$	Total conden- sable products
atm.	°C.	min.							
15	315	3.0	16.0	19.4	1.9	4.5	Nil	Nil	41.8
50	294	3.25	17.2	14.1	5.2	1.9	Nil	0.7	39.1
75	279	2.5	18.0	16.6	6.8	0.4	3.6	0.6	46.0
100	270.5	4.5	23.6	14.0	9.7	0.1	12.5	0.5	50.4

TABLE 6

*Products from the slow oxidation of ethyl alcohol at 100 atm. and 261°C.*

PARTIAL PRESSURE OF REACTANTS IN ATMOSPHERES			INITIAL TEMPERATURE	PRODUCTS AS PERCENTAGE OF THE ALCOHOL OXIDIZED OR DECOMPOSED								
C <sub>2</sub> H <sub>5</sub> OH	O <sub>2</sub>	N <sub>2</sub>		CH <sub>3</sub> CHO	CH <sub>3</sub> COOH	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub> OH	HCHO	HCOOH	CO <sub>2</sub>	CO	CH <sub>4</sub>
			°C.									
20	4	76	261	32.8	0.8	39.9	7.5		0.5	5.1	13.6	
20	10	70	261	20.7	2.4	36.2	13.5	0.2	0.3	20.4	3.6	2.6
10	10	80	261	10.4	1.4	35.6	8.2		0.4	27.6	12.5	
5	10	85	261	3.4	1.7	19.4	4.3	Trace	0.3	63.0	7.9	

the products are rapidly chilled, those initially formed should survive in increasing amounts. In this way it has been shown that at high pressures methyl and ethyl alcohols are formed at an early stage in the oxidation of methane and ethane, respectively (7). Furthermore, when methyl and ethyl alcohols are themselves oxidized at high pressures the products include all those found in comparable reactions with the parent hydrocarbons (table 6).

## OXIDATION OF PROPANE

Propane occupies a very important position between the lower and higher members of the paraffin series, for whilst its properties show certain resemblances to those of methane and ethane its reaction with oxygen is characterized by features peculiar to the higher hydrocarbons. The work of Prettre (10) and of Beatty and Edgar (1) has shown that during its slow combustion luminescence may be observed and in certain circumstances cool flames may be formed, whilst Townend and Chamberlain (12) have mapped out its upper and lower regions of inflammability.

*The reaction at high pressures*

When propane is oxidized at high pressures the products contain not only most of those intermediate substances found in the low-pressure

TABLE 7

*Products from the reaction of a 1:3.6 propane-air medium at 1, 20, 60, and 100 atm.*

Pressure in atmospheres.....		1	20	60	100
Reaction temperature in °C.....		373	281	252	250
PRODUCTS		PERCENTAGES OF THE CARBON OF THE PROPANE BURNED			
A	Total aldehydes.....	20.5	21.8	13.5	13.7
	Normal alcohols.....	19.7	21.0	17.5	15.2
B	Isopropyl alcohol.....	1.3	2.8	6.2	16.0
	Acetone.....	0.5	4.3	12.5	7.9
Acids.....		4.3	17.0	19.0	18.9
Carbon dioxide.....		7.3	17.1	21.4	20.6
Carbon monoxide.....		21.3	16.0	9.9	7.7
Propylene.....		25.1	Nil	Nil	Nil
Ratio A/B.....		22.3	6.0	1.7	1.2

reaction,—namely, propyl, ethyl, and methyl alcohols, propionaldehyde, acetaldehyde, and formaldehyde, and propionic, acetic, and formic acids,—but also isopropyl alcohol and acetone arising probably from some initial oxidation at the center  $-\text{CH}_2$  group (6). The rôle of pressure in inducing such a change in the primary process is by no means clear, but evidence suggests that it may be due to a change in polarity of the hydrocarbon molecule altering the ratio of the collision period leading to activation and the vibrational periods of the C—C or C—H linkages.

The effect of a progressive increase of pressure upon the distribution of products is well brought out by the data summarized in table 7, which relate to the reaction of a 1:3.6 propane-air medium at four pressures in the range 1 to 100 atm.

The most noticeable feature of these results is the absence of peroxidic bodies and of propylene in the high-pressure experiments and the increasing amount of isopropyl alcohol and acetone surviving as the pressure increases. If the sum of the total aldehydes and normal alcohols, A, and of the isopropyl alcohol and acetone, B, be taken as a rough measure of the tendency for oxidation to take place at a terminal methyl group and the central  $-\text{CH}_2$  group, then the progressive decrease in the ratio A/B indicates that the latter process is favored by pressure.

It has been shown that in the case of methane and ethane an increase in the concentration of the hydrocarbon favors the survival of liquid products, and propane behaves in a similar manner. Thus when a series of propane-air mixtures in which the proportion of propane is varied from 1:20 to 1:0.5 react at 30 atm. pressure and 275°C. in a static system, the

TABLE 8

*Products from the reaction of various propane-air mixtures at 30 atm. pressure and 275°C.*

Propane:air ratio.....		1:20	1:5	1:3.6	1:1.25	1:0.5
PRODUCTS		PERCENTAGES OF THE CARBON OF THE PROPANE BURNED				
A	Total aldehydes .....	12.5	8.8	12.0	16.1	16.7
	Normal alcohols.....	17.3	25.5	23.0	33.1	34.5
B	Isopropyl alcohol.....	2.7	6.9	5.2	5.2	14.4
	Acetone .....	1.2	1.4	1.3	0.3	7.4
Acids.....		13.9	13.4	15.2	8.9	12.5
Carbon dioxide.....		31.5	25.0	22.1	10.5	7.0
Carbon monoxide.....		20.9	19.0	21.3	25.9	8.0
Total condensable products.....		47.6	56.0	56.7	63.6	85.5
Ratio A/B.....		7.6	4.1	5.4	9.0	2.4

results given in table 8 are obtained. The total condensable products increase from 47.6 per cent for a 1:20 mixture to 85.5 per cent for a 1:0.5 mixture.

#### *The distribution of alcohols*

The normal alcohols formed during the slow combustion consist of methyl, ethyl, and propyl alcohols, methyl alcohol usually being present in excess (Pease (8)); the proportions in which they survive, however, depend upon the pressure, increasing amounts of propyl alcohol being found at the higher pressures. Thus, for example, Wiezevich and Frolich find that for an 11:1 propane-oxygen mixture, reacting at 170 atm. and 350°C., methyl, ethyl, and propyl alcohols are found in the approximate ratio 13.4:8:5.2, whilst Newitt and Schmidt (6) working with a propane-air



mixture at pressures between 5 and 65 atm. obtained the data given in table 9.

The formation of a series of normal alcohols from propane suggests that initial oxidation occurs at an end methyl group giving propyl alcohol, which then undergoes further oxidation *via* propionaldehyde to give in turn ethyl and methyl alcohols. In support of this view is the fact that propyl alcohol on oxidation at 240°C. and 56 atm. yields propionaldehyde, acetaldehyde, ethyl alcohol, and propionic and acetic acids, whilst ethyl alcohol at 280°C. and 50 atm. gives acetaldehyde, methyl alcohol, and acetic and formic acids. Propyl and ethyl alcohols are, however, more easily oxidized than is methyl alcohol, and consequently the latter would be expected to, and in fact does, survive in large quantities in the product.

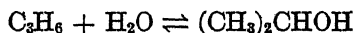
The increasing amounts of isopropyl alcohol and acetone found in the products as the combustion pressure is raised have been attributed to

TABLE 9

*Relative quantities of alcohols surviving from the slow reaction of a 1:3.6 propane-air medium*

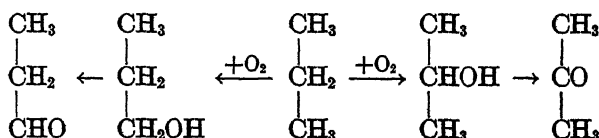
Pressure in atmospheres.....	5	30		65
PRODUCTS	PER CENT			
Methyl alcohol.....	76.3	58.0	55.3	50.1
Ethyl alcohol.....	19.1	17.6	13.2	9.8
Propyl alcohol .. . . .	4.6	4.3	7.3	12.2
Isopropyl alcohol.....		20.0	24.2	27.9

oxidation at the  $-\text{CH}_2$  group. An alternative view is that isopropyl alcohol might arise from hydration of propylene which occurs in large quantities during the low-pressure combustion. The reaction



however, requires the presence of a catalyst and the value of its equilibrium constant at 300°C. indicates that a considerable amount of propylene should be present in the system at equilibrium, whereas it is almost entirely absent in the high-pressure experiment.

It may therefore be concluded that the propane molecule can undergo oxidation in two ways according to the following scheme,



the proportions in which the oxygen is distributed depending upon the temperature, pressure, and the concentration of the reactants.

#### OXIDATION OF BUTANE

The products from the high-pressure oxidation of butane are too complex to admit of accurate quantitative analysis. Wiezevich and Frolich (14) have, however, identified acetaldehyde, propionaldehyde, acetone, acetic acid, propyl acetate, and methyl, ethyl, isopropyl, *n*-propyl, and isobutyl alcohols and give the data presented in table 10 to show the effect of pressure upon the types of products produced. Low pressure tends to favor the formation of lower alcohols and acids, and high pressure the formation of higher alcohols and aldehydes. The data are not sufficiently detailed to afford any indication as to the point of initial oxygen attack, although

TABLE 10  
*Products obtained in high-pressure oxidation of butane*

INLET OXYGEN GOING TO	PER CENT OF OXYGEN AT	
	33 atm.	133 atm.
Acetone .....	1.4	0.7
Methyl alcohol.....	15.0	8.4
Ethyl alcohol.....	2.5	6.3
Propyl alcohols. ....	3.2	8.9
Butyl alcohols.....	0.6	2.5
Aldehydes.....	6.9	15.9
Acids.....	16.7	4.6
Carbon dioxide.....	9.4	6.1
Carbon monoxide.....	3.8	9.4

the presence of isobutyl alcohol shows that some oxidation takes place at the  $-\text{CH}_2$  groups.

#### OXIDATION OF THE AROMATIC HYDROCARBONS

Although the controlled slow oxidation of the aromatic hydrocarbons forms the basis of a number of industrial processes such as, for example, the production of phthalic acid from naphthalene and of maleic acid from benzene, the actual mechanism by which ring cleavage occurs is still a matter of surmise. By carrying out such oxidations in the vapor phase at high pressure (4), however, comparatively low reaction temperatures can be employed and enhanced yields obtained of those nuclear derivatives formed in the primary processes before the ring breaks; in this way the successive steps in the initial phase of the oxidation of benzene, toluene, and ethylbenzene have been identified.

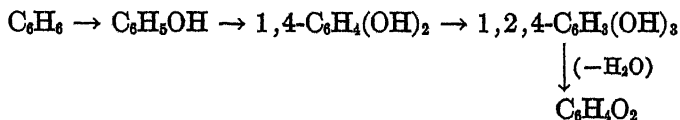
*Benzene*

The principal products from the oxidation of an excess benzene-oxygen medium in a static system at pressures of the order of 50 atm. are phenol, the two oxides of carbon, and steam. Smaller quantities of hydroquinone, quinone, maleic acid, and formaldehyde are also found, together with biphenyl, arising from the direct pyrolysis of the benzene. Unlike the reaction in the case of the aliphatic hydrocarbons, that of benzene is not preceded by any marked induction period and cool flames are not observed.

The yields of phenol from experiments at 312°C. with a series of mixtures in which the benzene-oxygen ratio was varied between 20:1 and 1.9:1, the partial pressure of the hydrocarbon being kept constant at 20 atm., are as follows (4):

Ratio C <sub>6</sub> H <sub>6</sub> :O <sub>2</sub>	Per cent of the C <sub>6</sub> H <sub>6</sub> burnt surviving as phenol
1.9	12.8
3.7	37.7
9.9	24.9
20.0	38.3

It is clear that an excess of the hydrocarbon is favorable to the survival of phenol. Similar results are obtained with benzene-air media, the products from a 4:1 mixture at 50 atm. and 362°C. being as given in table 11. The phenol recovered from this experiment represents upwards of 50 per cent of the benzene burnt. It is noteworthy that aromatic products other than phenol seldom survive in anything but traces in the homogeneous vapor-phase reaction; nevertheless the presence of hydroquinone and quinone (13) is significant in that it affords evidence that oxidation of the nucleus proceeds by successive stages of hydroxylation, as represented by the following scheme:

*Toluene and ethylbenzene*

The products of the oxidation of the simple alkyl derivatives of benzene may be divided into three groups, according as they result from oxidation of the nucleus, of the side chain, or of the fragments resulting from ring cleavage. The relative proportions in which each group survives depend *inter alia* upon temperature, pressure, and mixture composition. In the case of toluene the principal products are: (1) From side-chain oxidations, —benzyl alcohol, benzaldehyde, and benzoic acid; (2) from nuclear oxidation, —*p*-cresol and 2,4-dihydroxytoluene; (3) from ring cleavage, —ali-

phatic acids, formaldehyde, the two oxides of carbon, and steam. In addition bibenzyl is formed by the pyrolysis of toluene and small quantities of benzene from the decarboxylation of benzoic acid (4).

The proportions in which the more important of these substances are found in the products from a series of toluene-oxygen mixtures at 20 atm. reacting in a static system are shown by the results in table 12. It is evident that the course of the combustion and particularly the extent to

TABLE 11

*Oxidation of a 4:1 mixture of benzene and air at 50 atm. and 362°C.*

PRODUCTS	PERCENTAGE DISTRIBUTION OF OXYGEN
Phenol.....	10.6
Hydroquinone and quinone.....	Trace
Maleic acid.....	2.8
Formaldehyde.....	3.0
Carbon monoxide.....	26.2
Carbon dioxide.....	29.8
Water.....	27.6

TABLE 12

*Products from the reaction of various toluene-oxygen mixtures at 20 atm.*

INITIAL MIXTURE $C_6H_5CH_3$ : $O_2$	REACTION TEMPERATURE IN °C.	PRODUCTS AS PERCENTAGES OF THE CARBON OF THE TOLUENE BURNT						PERCENTAGE DISTRIBUTION OF OXYGEN IN	
		Benzyl alcohol	Benzaldehyde	Benzoic acid	2,4-Di-hydroxy-toluene	$CO_2$	CO	Side chain	Nucleus
30*	337	6.2	50.6	16.3	9.9	5.2	5.4	81.5	18.5
20*	276	5.9	36.1	12.1	14.7	3.0	1.4	71.0	29.0
3.7	250	2.8	21.9	26.2	6.1	17.9	6.0	86.5	13.5
3.2	250	1.6	18.1	53.0	6.3	18.3	4.7	91.0	9.0
1.5	250	1.2	8.6	47.1	5.1	19.6	3.8	91.0	9.0
1.0	250	0.7	3.0	59.3	7.1	25.8	3.8	89.5	10.5

\* These mixtures contained 3.76 atm. of nitrogen.

which the side chain undergoes oxidation are influenced to a very marked degree by the composition of the medium. Thus whilst the comparatively rich 1:1 toluene-oxygen mixture gave 59.3 per cent of benzoic acid in the products and only 3 per cent of benzaldehyde and less than 1 per cent of benzyl alcohol, the 30:1 mixture gave 6.2 per cent of benzyl alcohol, 50.6 per cent of benzaldehyde, and only 16.3 per cent of benzoic acid. In the case of the latter mixture no less than 83 per cent of the carbon of the toluene burnt appeared as aromatic intermediates in the products.

The reaction temperature has also a considerable influence upon the distribution of the products, as may be seen from the data in table 13, relating to two mixtures containing toluene and air in the proportions of 20:5 and 30:5, respectively, the partial pressure of oxygen being 1 atm. An important feature of these results is the progressive increase in the amount of benzyl alcohol surviving with increase of temperature, together with a corresponding decrease in benzoic acid. It is evident that by suitably adjusting the temperature and the hydrocarbon-oxygen ratio any one of the three side-chain derivatives can be obtained in high yields relative to the amount of hydrocarbon consumed.

TABLE 13

*Products from the combustion of 20:5 and 30:5 toluene-air mixtures at various temperatures*

TEMPERATURE IN °C.	PRODUCTS AS PERCENTAGES OF THE CARBON OF THE TOLUENE BURNED					
	Benzyl alcohol	Benzalde- hyde	Benzoic acid	2, 4-Di- hydroxy- toluene	CO <sub>2</sub>	CO
20 C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> + 5 air						
276	5.9	36.1	12.1	14.7	3.0	1.4
304	5.6	38.6	17.7	15.0	3.5	3.0
331	6.0	4.04	19.4	17.9	4.5	3.8
375	15.8	30.0	10.2		14.4	5.3
400	31.1	30.1	8.1	10.2	14.7	4.2
30 C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> + 5 air						
337	6.2	50.6	16.3	9.9	5.2	5.4
358	8.3	45.4	10.6	10.7	4.0	5.5
391	16.6	31.0	9.7	9.3	4.2	3.9
503*	6.6	3.2	3.6	3.9	3.5	9.8

\* Inflammation occurred with carbon deposition.

### *Ethylbenzene*

In the liquid phase ethylbenzene combines readily with oxygen at temperatures of 100–120°C. giving acetophenone and the oxides of carbon but no alcohol or aldehyde (11); in the presence of a manganese oxide catalyst, however, methylphenylcarbinol, benzoic acid, and formaldehyde are found in addition to the above products (2). In discussing the mechanism of the reaction Stephens concludes that the hydrogen attached to the carbon atom in the alpha position is first removed and that oxygen tends to substitute in the same position as do the halogens, giving acetophenone; the alcohol is regarded as arising from some independent secondary reaction.

Newitt and Burgoyne, on the other hand, have studied the vapor-phase combustion and show that reaction in these circumstances takes place by successive hydroxylations of the hydrogen attached to the carbon atom in the alpha position, yielding as a primary product methylphenylcarbinol, which in turn gives acetophenone. The further oxidation of acetophenone occurs by hydroxylation of the hydrogen attached to the carbon in the beta position, giving benzaldehyde and benzoic acid. At the same time some direct oxidation of the nucleus takes place, giving as the main product 2,4-dihydroxyethylbenzene.

As an example of their results the data of table 14 relating to a 20:7.5 ethylbenzene-air mixture reacting at 27.5 atm. and 322°, 385°, and 437°C., respectively, may be given. The increase in the methylphenylcarbinol with increase of reaction temperature affords evidence that it constitutes the initial product of the oxidation. The above experiments also show that with rise of temperature there is an increasing tendency for the nucleus

TABLE 14

*Products from the combustion of a 20:7.5 ethylbenzene-air medium at 27.5 atm.*

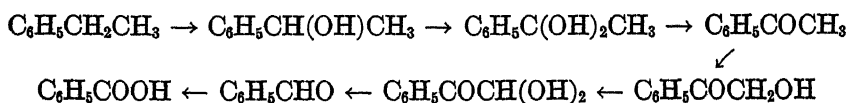
Reaction temperature in °C. . . . .	322	285	437
PRODUCTS	AS PERCENTAGES OF THE CARBON OF THE ETHYLBENZENE BURNED		
Methylphenylcarbinol.....	8.9	11.5	27.7
Acetophenone.....	13.4	Trace	Trace
Benzaldehyde .....	54.0	52.3	23.6
Benzoic acid. ....	6.4	8.9	8.7
2,4-Dihydroxyethylbenzene...	10.3	9.2	6.8

to undergo direct oxidation, the distribution of oxygen between the side chain and the nucleus at the three temperatures being as follows:

TEMPERATURE IN °C.	PER CENT DISTRIBUTION OF OXYGEN IN	
	Side-chain products	Nuclear products
322	77.0	23.0
385	75.0	25.0
437	69.0	31.0

Although the formation of benzaldehyde and benzoic acid has been attributed to further oxidation of acetophenone, they might equally well arise from ethylbenzene by successive hydroxylations of the hydrogen attached to the carbon in the beta position. In this event phenylethylalcohol should be the first step in the oxidation and should be detectable in the

products; no trace of it, however, has ever been found, whilst experiments with acetophenone show that on oxidation considerable amounts of benzaldehyde and benzoic acid are formed. The intermediate stages in the oxidation of ethylbenzene would therefore appear to be:



#### SUMMARY AND CONCLUSIONS

A general survey of the experimental data relating to the combustion of both the aliphatic and the aromatic hydrocarbons makes it clear that pressure exerts a well-defined influence on the course of the reactions involved. It has been shown in the foregoing pages that it accelerates the rate of reaction, exerts a directive action on the primary oxidation

TABLE 15  
*Effect of pressure upon the rate of reaction*

HYDROCARBON	TEMPERATURE AT WHICH OXIDATION IS FIRST DETECTABLE WHEN THE PRESSURE IS			
	1 atm.	50 atm.	100 atm.	150 atm.
Methane. ....	420	350	330	320
Ethane. ....	285	276	260	
Propane. ....	270	255	245	232
Butane. ....		248	220	210
Benzene. ....		270	260	
Toluene. ....		210	195	

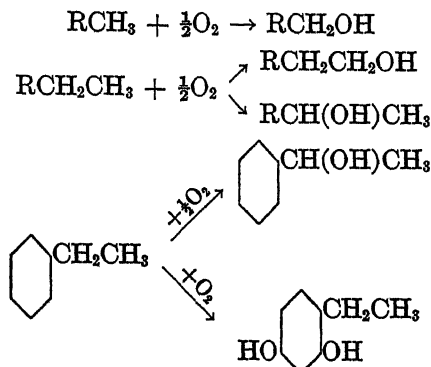
process, and influences to a marked degree the distribution of the oxygen in the products. In all cases of pressure oxidation in which oxygen is in defect the products have been shown to contain large quantities of normal alcohols or phenolic derivatives arising at some early stage of the oxidation. Thus it is possible to burn methane under conditions which give yields of methyl alcohol of upwards of 50 per cent, and similar results are obtained with ethane, propane, benzene, and toluene.

With the higher aliphatic hydrocarbons another pressure effect of importance is the change in the point of oxygen attack on the molecule; there is an increasing tendency with rise of pressure for direct oxidation to occur at some midpoint in the chain giving iso-alcohols and ketones, the change being probably attributable partly to the increase in the collision factor and partly to a change in the polarity of the molecule due to close packing.

The alkyl derivatives of benzene show a somewhat similar behavior, for whilst the side chains are more open to attack and at atmospheric

pressure appropriate all the oxygen, at high pressures the nucleus and side chains undergo simultaneous oxidation.

Without entering into any discussion involving the kinetic aspects of the various oxidations, there is evidence from the analytical results that the initial stages of the process taking place at high pressures are represented by the following scheme:



The effect of pressure is generally to increase the rate of reaction, as may be seen from the comparative figures in table 15.

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#### DISCUSSION<sup>1,2</sup>

BERNARD LEWIS AND GUENTHER VON ELBE: Dr. Newitt has interpreted his results in terms of initial hydroxylation. It appears to us that a

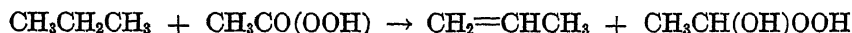
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<sup>2</sup> Received September 25, 1937.

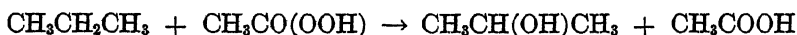


scheme based on a chain mechanism involving chain carriers of the peroxide type would do more justice to his results. This has already been outlined by us in the case of the oxidation of methane and ethane at high pressures (J. Am. Chem. Soc. **59**, 976 (1937); *Combustion, Flames and Explosions of Gases*, Cambridge University Press (1938)). In particular, the radical chain allows a ready interpretation of the yields of methyl and ethyl alcohols in the oxidation of ethane. It is not difficult to account for all the observed products and the trends of their yields with varying temperature, pressure, and mixture composition.

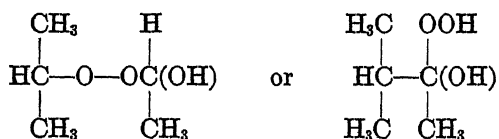
Among his newer results on the oxidation of propane we note, in particular, the simultaneous appearance of isopropyl alcohol, acetone, and acids and the disappearance of propylene and peroxides as the reaction temperature is lowered and the pressure increased. This reaction may be understood from our previously proposed formation of oxy-alkyl peroxides and olefins by reactions between peracids or their radicals and paraffins. At lower temperatures this reaction is easily conceived to take a somewhat different course than at higher temperatures. Thus, at high temperatures the following reaction might be favored:



Low temperatures would favor



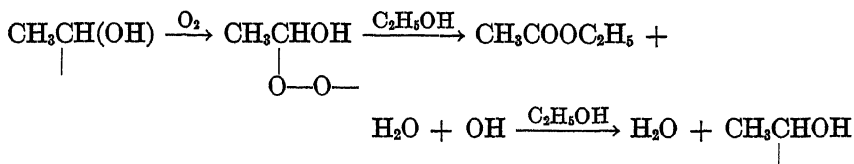
It is possible that the primary step in the above two reactions is a condensation of the hydrocarbon and peracid to form



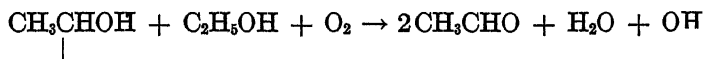
which then split up into the products noted at different temperatures.

The acetone could be formed in a subsequent step from isopropyl alcohol, for example, by a reaction with a peroxide.

Another example that may be mentioned is the oxidation of ethyl alcohol at high pressures. The lower the percentage of oxygen in the mixture, the larger the yields of acetaldehyde. The yield of ethyl acetate, which is one of the main products, is much less susceptible to change in mixture composition. The formation of the latter substance is readily represented by a radical chain, viz.



If at constant pressure the percentage of oxygen is decreased, the number of binary collisions between alcohol *radical* and oxygen should decrease relative to the number of ternary collisions



thus leading to larger yields of acetaldehyde.

Regardless of the correctness of these particular schemes, we believe that a consistent interpretation of the oxidation of hydrocarbons is possible only along these lines.



# THE MECHANISM OF THE COMBUSTION OF HYDROCARBONS<sup>1</sup>

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The purpose of this paper is to present a critical comparison of recent theories suggested by Norrish and Foord (6), Ubbelohde (13), Jost and coworkers (4), Pease (7), Semenoff (12), and von Elbe and Lewis (14) for the mechanism of the combustion of hydrocarbons. The subject may be divided into the chemical mechanism and the kinetics of the oxidation. A detailed description will not be presented, the object being to discuss viewpoints on subjects touched on by several authors.

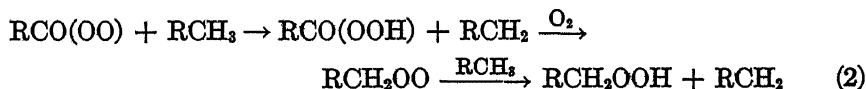
## THE CHEMICAL MECHANISM

### *The unbranched-chain reaction*

It is generally agreed that the oxidation of hydrocarbons occurs by a chain mechanism and that aldehydes appear as intermediates. Both Ubbelohde and von Elbe and Lewis formulate the chain reaction on the basis of evidence obtained in the oxidation of aldehydes. The latter reaction is also of the chain type, and it is reasonable to assume that both the above chain reactions are interdependent. Ubbelohde follows Bäckstrom's (1) mechanism by which the aldehyde oxidation chain is initiated by the formation of a radical RCO which then reacts according to the scheme:



According to Ubbelohde, in the presence of a paraffin hydrocarbon



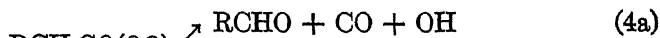
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The alkyl peroxide undergoes decomposition



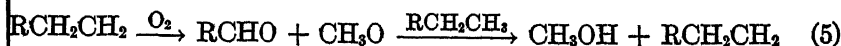
a reaction of which the peroxide radical may also be capable, to give either aldehyde and OH or aldehyde radical and  $\text{H}_2\text{O}$ . Such suggestions are also advanced by Jost and coworkers. For the formation of the main oxide of carbon, namely carbon monoxide, Ubbelohde, as well as Jost, proposes the subsequent decomposition of the aldehyde formed in reaction 3, or of the aldehyde radical formed in reaction 1, leaving the saturated hydrocarbon or hydrocarbon radical, respectively. As a side reaction, Ubbelohde proposes the occasional transformation of the hydrocarbon radical into olefin and hydrogen atom; this, however, is a strongly endothermic process. Having shown experimentally the formation of oxygen ring compounds in the higher paraffin series, he arrives at a simple mechanism for such ring formation from peroxide radicals. Furthermore, the formation of alcohols at high pressures is accounted for by the interaction of two peroxide radicals to yield two molecules of alcohol and  $\text{O}_2$ .

von Elbe and Lewis arrive at Bäckstrom's mechanism (reaction 1) from the following independent evidence. In the photochemical decomposition of aldehydes, monovalent radicals are formed; in the photooxidation of aldehydes higher than formaldehyde, peracids are formed by a chain mechanism. These two facts alone make reaction 1 the only plausible one, and in addition this mechanism correctly describes the dependence of the yield on light intensity and concentrations of reactants. According to von Elbe and Lewis, the decomposition of aldehydes or their radicals into carbon monoxide and hydrocarbon or radical is not plausible. This is shown particularly by the experiments of Pope, Dykstra, and Edgar (8) on the thermal decomposition of aldehydes. However, it is very plausible that the peracid or its radical should decompose at the high temperature, for example, according to the scheme:

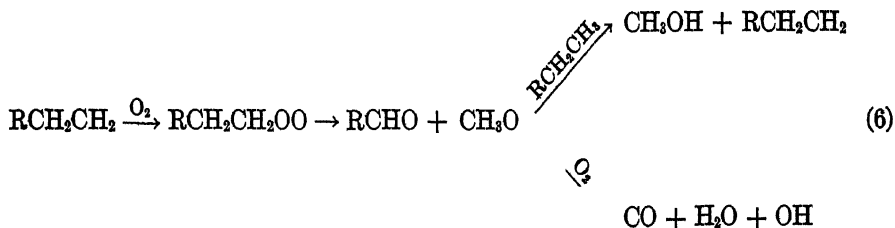


This would agree with Pope, Dykstra, and Edgar's overall "degradation" reaction which in normal paraffins ultimately leads to formaldehydes and which in iso-paraffins is interrupted at the ketone stage (9). Various possibilities of this interruption have been discussed by Jost.

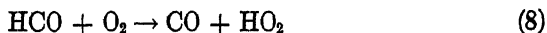
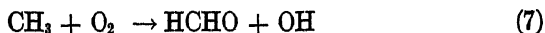
For the oxidation of an alkyl radical, Pease proposed the following chain instead of the second and third steps in reaction 2,



since he observed the formation of large amounts of methyl alcohol at moderate temperatures in rich mixtures of propane and oxygen. In order to reconcile this mechanism with the probable appearance of alkyl peroxides as proposed by Ubbelohde, which is made plausible by the appearance of a low-temperature branching reaction (see below), and with the absence of methyl alcohol in lean mixtures of propane and oxygen, von Elbe and Lewis introduced the following modification of reaction 5:



If the alkyl radical is  $\text{CH}_3$ , a direct association with  $\text{O}_2$  is very improbable, as is indicated by the work of Kimball (5). This also applies to the formaldehyde radical  $\text{HCO}$ . Therefore, for ordinary pressures, von Elbe and Lewis postulate



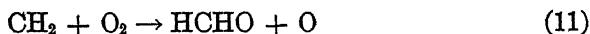
$\text{HO}_2$  reacting according to



In the oxidation of rich mixtures of methane at high pressures  $\text{CH}_3\text{OO}$  may be formed in three-body collisions and give rise to methyl alcohol by various reactions, involving presumably the primary condensation of methyl peroxide or its radical with formaldehyde, followed by dissociation at the peroxidic bond. This corresponds to the peroxide studies of Rieche and coworkers (10). This hypothesis proves to be fruitful in accounting not only for the experimental facts connected with the high-pressure oxidation of methane and ethane, but also for the low-temperature branching of higher paraffins (see below). In particular, in the high-pressure reaction the effect of mixture composition on the alcohol yields is explained by the susceptibility to oxidation of the alkoxy radical as in reaction 6. The suggestions of Jost and coworkers concerning alcohol formation at high pressures are not far removed from the above: A ternary collision between alkyl radical,  $\text{O}_2$ , and hydrocarbon molecule is postulated to lead either immediately to alcohol and alkoxy or to alkyl peroxide and

an alkyl radical, the peroxide to dissociate into OH and alkoxy, the latter giving rise to alcohol.

Norrish's chain mechanism is based entirely on the alternate appearance of oxygen atoms and alkylene radicals which, for methane, he writes



and for formaldehyde oxidation as an unspecified chain mechanism involving oxygen atoms. At high pressure, oxygen atoms are assumed to combine with hydrocarbons in a three-body collision to form alcohols. The reaction constitutes a chain-breaking process in the gas phase which is of the first order with respect to the chain carrier. A similar chain-breaking process with monovalent radicals is impossible. A number of objections to the oxygen atom mechanism have been advanced by Ubbelohde, Jost, and von Elbe and Lewis, among which two may be mentioned here. If oxygen atoms are introduced into hydrocarbons at room temperatures, emission of the band spectra of  $\text{C}_2$ , CH, and OH occurs; that is, radicals appear possessing a different number of free valences than the oxygen atom. In the slow oxidation of methane these spectra are not emitted. Instead there is the fluorescence spectrum that has been found to arise from excited formaldehyde. If oxygen atoms were participating in the mechanism, the absence of bands of  $\text{C}_2$ , CH, and OH would be difficult to explain. A second objection is that a reaction between an oxygen atom or a bivalent radical with a saturated molecule can easily be conceived as leading to two monovalent radicals which should exhibit the properties of chain carriers. The reverse process—namely, the formation of bivalent from monovalent radicals—would require the reaction of two monovalent radicals, which would be a very rare event in view of their low concentration.

The view is generally accepted that at ordinary pressures chains are broken principally at the wall.

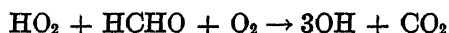
### *Chain branching*

The low-temperature reactivity and explosivity of higher hydrocarbons can be explained by assuming a branching reaction with an optimum probability in a certain temperature range. Ubbelohde suggests branching to occur on collision of an energy-rich peroxide with hydrocarbon to yield water, alkyl radicals, and alkoxy radicals or to occur in a triple collision between two hydrocarbon molecules and a peroxide radical to yield two alkyl and one alkoxy radicals. Assuming the lifetime of the peroxide molecule or its radical to be limited by the decomposition reaction (3) and to be shorter the higher the temperature, branching is favored at

lower temperatures. Essentially the same idea is proposed by Jost. On the other hand, von Elbe and Lewis propose a branching reaction which had already successfully accounted for the alcohol yields in the high-pressure reactions and was supported by the chemistry of peroxides. According to this, the breaking of the peroxidic bond is sensitized by the condensation of the peroxide or its radical with aldehyde. This branching mechanism accounts for the influence of aldehyde on the low-temperature explosion peninsula, which is not described by the alternative branching mechanisms of Ubbelohde and Jost. The branching probability is largely determined by the lifetime of the peroxide radical, which is governed by a decomposition reaction analogous to reaction 3. The absence of a low-temperature explosion peninsula in methane is easily understood by the inability of methyl radicals to form methyl peroxide radicals except in triple collisions. The gradual disappearance of the low-temperature explosion peninsula in higher paraffins having more condensed structures is again connected with their decreasing ability to form aldehydes.

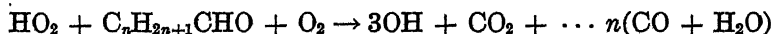
The oxygen atom mechanism of Norrish apparently does not admit a similar set of plausible competing reactions.

The explosion limit of methane and the high-temperature explosion limits of higher hydrocarbons can be explained, according to von Elbe and Lewis, by another branching reaction:

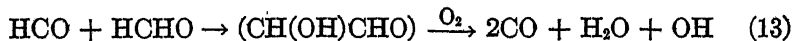


or

(12)



competing with a reaction involving primary formaldehyde condensation, namely,



The necessity for introducing reactions of this kind depends on whether one considers the high-temperature explosion to be of the thermal or branched-chain type. This will be discussed below.

#### KINETICS

##### *The steady-state rate*

Detailed kinetic treatments are to be found in the work of Norrish and Foord, which is confined to methane, and in the work of von Elbe and Lewis. Both treatments are based on the production of chain carriers by aldehyde, assumed to be a homogeneous reaction by Norrish and Foord and a heterogeneous reaction by von Elbe and Lewis, and the destruction and production of aldehyde by chain mechanisms. Since in von Elbe and



Lewis' treatment the concentration of formaldehyde at the surface is assumed to be proportional to the gas-phase concentration, both mechanisms are kinetically equivalent, except for the homogeneous alcohol-forming chain-breaking reaction of Norrish and the branching reactions of von Elbe and Lewis. For the case of negligible branching and neglecting the alcohol-forming reaction, the steady-state rate following the establishment of the maximum aldehyde concentration is in both cases proportional to the square of the hydrocarbon concentration and the first power of the oxygen concentration. If aldehyde forms chain carriers in the gas phase, then for a chain-breaking efficiency of the wall that is large compared with the ratio of the mean free path to vessel diameter, the reaction rate is proportional to the total pressure and the proportionality factor in the rate equation is independent of the nature of the surface (15). If the chain-breaking efficiency is small compared with the above ratio, the rate becomes inversely proportional to the chain-breaking efficiency, but the additional pressure factor in the rate equation disappears (15). In the first of the above cases the rate is proportional to the square of the diameter and in the second case to the first power of the diameter.

If aldehyde forms chain carriers at the wall, no additional pressure factor enters into the rate equation, and the proportionality factor always depends on the nature of the surface (15). As long as branching is negligible the rate is independent of diameter.

The pronounced effect of surface on the rate rules out the first case under the formation of chain carriers from aldehyde in the gas phase. Concerning the second case, it is not very probable that vessels having walls of extremely low chain-breaking efficiencies should have been used by all investigators. According to the theory, a decision between the second and third cases (formation of chain carriers from aldehyde at the wall) should be possible by investigating the diameter dependence of the rate. In ethane-oxygen mixtures at low pressures (a few centimeters of mercury) and at about 600°C. in silica vessels etched with hydrofluoric acid, the rate has been found to be independent of diameter (11). The experiments were well reproducible, pointing to the conclusion that etching produces a more or less uniform and stable surface. In unetched vessels the results were erratic. Norrish and Foord investigated the effect of diameter on the rate in untreated cylindrical Pyrex vessels at 530°C. in the pressure range 150 to 300 mm. of mercury. They find a mild diameter dependence between diameters of 7.5 mm. to 37.5 mm., although for small vessels they find a sharp drop in the rate. Before any conclusions are drawn from these results, the influence of pressure should be mentioned.

At a constant total pressure of about 1 atm. and at 447°C., Bone and

Allum (2) found that a mixture containing 66.7 per cent of methane in oxygen reacted faster than mixtures containing 50 or 75 per cent of methane. At 467°C. and at pressures ranging from 300 to 600 mm., Fort and Hinshelwood (3) found the rate to depend on a power of the methane concentration exceeding 2 and a power of the oxygen concentration exceeding 1. At 480°C. and presumably up to atmospheric pressure, Norrish and Foord found approximate proportionality of the rate to the product  $(\text{CH}_4)^2P$  at constant oxygen pressure and to the product  $(\text{O}_2)P$  at constant methane pressure. They also added nitrogen to 250 mm. of methane and 100 mm. of oxygen up to a total pressure of about 800 mm. and found approximate proportionality of the rate to total pressure.

Of these results, those of Bone and Allum are most readily interpreted by the fact that the product  $(\text{CH}_4)^2(\text{O}_2)$  reaches a maximum at 66.7 per cent methane. The other observations on the influence of total pressure are predicted neither by case 2 nor by case 3 unless one grants that the chain-breaking efficiency of the wall is inversely proportional to the pressure. This is not inconceivable if one considers the possible influence of adsorbed gas layers on the wall. It is also possible that aldehyde produces chain carriers both by a heterogeneous and by a homogeneous reaction with oxygen, the former predominating at lower pressures and the latter at higher pressures. One would then expect some intermediate case between 1 and 3, thus allowing for the influence of the nature of the surface, the diameter dependence, and the pressure factor.

There is still one other possibility which was specifically considered by von Elbe and Lewis (14), that is, case 3 obtains and chain branching is not negligible. The branching term would introduce a diameter dependence and a pressure factor of variable orders depending on the relative magnitudes of the chain-breaking and chain-branching rates. Experiments have not been sufficiently extensive to rule out the necessity for such flexibility.

Norrish and Foord do not fully apply the diffusion theory, in that they assume the rate of chain breaking always to be proportional to a factor  $S/Pd$ ,  $S$  being the surface activity per unit area,  $P$  the total pressure, and  $d$  the diameter of the vessel. Therefore they have not fully treated the complex problem of accounting simultaneously for the influence of pressure, diameter, and nature of the surface. Strictly within their own picture, the chain-breaking rate should be proportional to  $1/Pd^2$  for efficiencies large compared to the ratio of the mean path to diameter and proportional to  $S/d$  for efficiencies small compared to this ratio. In the former, the influence of the nature of the surface would have had to be sacrificed and a fairly powerful diameter dependence introduced; in the latter, the pressure factor would have had to be sacrificed.

*The explosive reaction*

In the treatments of Norrish and Foord and of von Elbe and Lewis aldehyde is both created and destroyed by chain carriers. The rate of production of formaldehyde is at first a very slow process, because the concentration of chain carriers is very small. Its rate of destruction is still smaller, because the aldehyde concentration is also very small. Assuming that the production of new chain carriers by aldehyde is a rare event, one can appreciate the rather long induction periods during which the aldehyde concentration increases, until finally it becomes comparable in magnitude to the concentration of hydrocarbon (of the order of 1 per cent) and the rates of formation and destruction of aldehyde approach equality. The reaction rate then reaches its steady-state value. Norrish and Foord believe that explosion occurs if this maximum rate is sufficiently fast to destroy the thermal equilibrium. They link their theory to the Semenov theory of "degenerate" branching (12). The latter author's views, however, differ from those of Norrish and Foord and of von Elbe and Lewis in that the intermediate product, which presumably must be identified with aldehyde, is oxidized to the final products independently, that is, without reacting with a chain carrier. Thus, if the concentrations of the reactants, hydrocarbon and oxygen, remained constant, there would be a steady accumulation of the intermediate product and consequently a continuous acceleration of the reaction rate due to production of new chain carriers by aldehyde. The rate would never reach a steady state and only exhaustion of the reactants would slow it down. From a chemical point of view, this course of the reaction is hardly conceivable, because it is known that aldehyde is oxidized by a chain reaction. Semenov's support for his argument, namely, that the inflection point in the rate curve occurs at a high percentage of the total reaction, is not borne out by the experiments of Norrish and Foord. It should also be mentioned that without prejudicing the steady-state theory, a constant reaction rate cannot actually be observed during the course of the reaction because the effect of exhaustion of the reactants should occur early, so that the non-explosive reaction will always consist of a period of acceleration followed by a period of deceleration.

There remains the question whether the explosion is of the thermal type (Norrish and Foord) or of the branched-chain type (von Elbe and Lewis). There are no certain simple criteria to decide this question. Only the upper explosion limits of such mixtures as hydrogen or carbon monoxide and oxygen can be ascribed, with some assurance, to chain branching. In the present case, thermal and branched-chain theories both demand a continuous acceleration of the reaction on approaching the explosion limit by the change of any experimental variable. It is not justifiable to give

preference to either theory from observations of this type, unless the observations can be made accurately and quantitatively and compared with a quantitative theory. Neither theory nor experimental technique has developed to this stage.

Norrish and Foord base their preference for the thermal character of the explosion on their observation that the induction periods, measured in the non-explosive region up to maximum reaction rate and in the explosive region up to ignition, lie on a continuous curve when plotted against total pressure. However, this result is also consistent with the branched-chain theory.

Although the reaction rate depends rather strongly on the nature of the surface, the branched-chain theory (15) demands that the explosion limit be relatively unaffected by the nature of the surface unless the chain-breaking efficiency is small compared with the ratio of the mean free path to vessel diameter. Actually, the limit is found to be influenced somewhat by the nature of the surface. Assuming that the chain-breaking efficiency is large compared with the above-mentioned ratio, this does not rule out the possibility that the limit is essentially governed by a chain-branching mechanism and that it is lowered somewhat by a thermal factor which enters in by virtue of the acceleration of the reaction rate near the limit.

von Elbe and Lewis base their preference for the branched-chain theory of the explosion on the effect of mixture composition on ignition temperature. Whereas the maximum reaction is at a mixture composition of about 66.7 per cent methane in oxygen, the minimum ignition temperature has been found for a mixture containing about 33 per cent methane. Judging from the change of the product  $(\text{CH}_4)_2(\text{O}_2)$  and the change in thermal conductivity of the mixtures, this shift of optimum composition appears entirely too large to be accounted for by the thermal theory in connection with the proposed chain mechanism of the slow reaction, and to require the introduction of an additional mechanism which is readily conceived of as a branching mechanism. The argument is strengthened still further by the effect on the minimum ignition temperature of substituting helium for argon as diluent in methane-oxygen mixtures. Keeping the total pressure constant one would expect, on the basis of the purely thermal theory, the minimum ignition temperature in helium mixtures to shift to a larger ratio of methane to oxygen as compared to argon mixtures, because the larger heat conductivity of the former mixtures would require a faster reaction to destroy the thermal equilibrium. Actually the reverse is true, the minimum ignition temperature in helium mixtures being shifted toward smaller ratios. The branched-chain mechanism as proposed by von Elbe and Lewis accounts for these and related facts.

## SUMMARY

Recent theories of hydrocarbon oxidation have been critically compared. The evidence favors monovalent radical chains. The assumption of intermediate formation of peroxides and of sensitization of peroxide dissociation by condensation with aldehyde proves to be fruitful in explaining varied phenomena, such as the low-temperature reactivity of higher hydrocarbons and the high-pressure oxidation of methane and ethane. The implications of the chain theory in interpreting the experimental results have been discussed. The necessity of revising Norrish and Foord's steady-state treatment has been pointed out. The question of thermal versus branched-chain explosions in methane remains open, with some experimental evidence favoring the latter.

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DISCUSSION<sup>2</sup>

HAROLD A. BEATTY (Ethyl Gasoline Corporation, Detroit, Michigan): The pioneer work of Pope, Dykstra, and Edgar (*J. Am. Chem. Soc.* **51**, 2203 (1929)) on the slow oxidation of branched-chain octanes suggested that a step-wise degradation of the longest straight chain takes place until a secondary carbon atom is reached, at which point a stable ketone is formed. This suggestion has been more or less accepted as a specific fact by subsequent investigators, without its having been put to experimental proof. Actually, the results of some previously unpublished work by the author in 1931 on the slow oxidation of 2,5-dimethylhexane indicate that the overall reaction is by no means as simple as was originally suggested.

<sup>2</sup> Received September 25, 1937.

Using the conventional flow method (Beatty and Edgar: J. Am. Chem. Soc. **56**, 102 (1934)) it was found that the oxidation of this octane in air starts at a low temperature, 235°C. At 346°C. the reaction is very fast, the temperature near the inlet being 74°C. above that of the thermally uniform portion of the furnace, 272°C., and it may safely be assumed that 75 to 100 per cent of the hydrocarbon is partially oxidized. Holding this temperature constant, 17.40 g. of the hydrocarbon was oxidized in 635 min. at a molal oxygen/fuel ratio of 9.6.

Analysis of the gaseous products uncondensed at -78°C. gave, per mole of hydrocarbon input, 2.30 moles of oxygen used, and 0.73 mole of carbon monoxide, 0.10 mole of carbon dioxide, and 0.08 mole of unsaturated gas (probably ethylene) formed. The liquid condensate weighed 23.44 g., giving a total recovery of 99.9 per cent. It contained, per mole of hydrocarbon input, 1.80 moles of water and about 0.2 mole of acid, principally formic acid. So far this is in fairly good agreement with the suggested mechanism of oxidation to 5-methylhexanone-2.

However, the aqueous condensate,  $d = 1.05$ , weighed 11.4 g. of which only 40 per cent was water; aldehyde and acetone were present in quantity. The upper layer,  $d = 0.84$ , weighing but 12.0 g., had a boiling range from below 90°C. to above 155°C. The fraction boiling below 100°C., 3.6 g., gave a strong test with Schiff's reagent, and yielded a *p*-nitrophenylhydrazone melting at 142.5–143.5°C., with a molecular weight of about 200 to 225, apparently not a single compound. The fraction boiling from 115°C. to 155°C., 3.1 g., gave negative tests with sodium, sodium bisulfite, and semicarbazide, and a trace of oil with *p*-nitrophenylhydrazine; certainly none of the expected ketone was present.

This analysis is admittedly far from complete, but it serves its purpose to the extent of showing definitely that a certain amount of extensive degradation or rupture of the carbon chain takes place, and that no 5-methylhexanone-2 appears in the products. It seems, therefore, that while the original suggestion is probably valid in principle, it cannot be accepted literally or specifically, and each individual branched-chain hydrocarbon will have to be considered, to a certain extent, as an isolated problem.



# THE MECHANISM OF THE COMBUSTION OF HYDROGEN

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*Received July 14, 1937*

## INTRODUCTION

The combustion of hydrogen, in common with that of the other fuels dealt with in this symposium, may occur either as a slow reaction or as an explosion, depending upon the experimental conditions. This paper will treat these two main types of reaction separately. The reaction kinetic interpretation of the foregoing phenomena will constitute the third and final section. The space available does not permit anything like complete discussion of a reaction which even in 1934 could be the subject of a 100-page monograph (17), and many aspects of the reaction will be omitted entirely.

## THE SLOW REACTION

The reaction between hydrogen and oxygen may be brought about catalytically by a variety of metallic surfaces. These catalytic reactions have been carefully studied in a number of cases, and have given interesting information concerning the relative adsorption of hydrogen, oxygen, and steam on the surfaces involved. The temperature of these reactions is so low, however, that they are almost totally unrelated to the phenomena of combustion as the term is usually understood, and they will therefore not be discussed in the present paper.

A catalytic reaction is found even with ordinary silica or porcelain reaction vessels. This catalysis, however, is far feeblower than that by most metals, the rate being easily measured in a static system at 520°C. This reaction is approximately of the first order with respect to hydrogen, nearly of the zero order with respect to oxygen (except at quite low partial pressures), and retarded by steam. This catalysis can only be observed when the pressure is sufficiently high; at lower pressures there is a more or less instantaneous explosion, the nature of which is dealt with in the following section. When experimentation is confined to pressures above this explosion limit, very striking changes in the reaction kinetics are observed as the temperature is raised. Below about 540°C. the reaction is of low order, has a low temperature coefficient, is retarded by steam, and is



accelerated in a packed vessel. At slightly higher temperatures the reaction is of high and variable order (about fourth), has a very high temperature coefficient, and is accelerated by steam or other inert gases and retarded in a packed vessel. There is no reason to doubt that the low-temperature surface reaction continues into this range with the characteristics that would be predicted for it by extrapolation. The changed kinetics are due to a quite new reaction, taking place predominantly in the gas phase, which becomes much faster than the surface reaction. This gas reaction can be studied only for a narrow range of conditions. The pressure must be above the previously mentioned explosion limit, and below a second (or, more precisely, as develops later, a third) limit. These limits come together as the temperature is raised and cut off the non-explosive reaction completely at about 580°C. Below about 550°C., on the other hand, the normal wall reaction is fast enough to obscure or even to obliterate the gas reaction.

The temperature coefficient of the homogeneous reaction increases with increase of both temperature and pressure. Values up to 4.3 for 10°C. at 560°C. are found, corresponding to an "activation energy" of 200 kg-cal. It will be seen in the third section, however, that there is no physical significance to the energy of activation for reactions of this type.

The gas reaction is of about the third order with respect to hydrogen and the 1.5 order with respect to oxygen (16, 12). The addition of nitrogen to a stoichiometric mixture increases the initial rate about linearly with the amount added, the increase being roughly the same as would be produced by an equal quantity of oxygen. Other inert gases behave similarly, the relative effectiveness of helium, nitrogen, argon, and water being in the ratio 1:3:4:5.

The rate is very markedly reduced by packing the reaction vessel. The effect of surface is best studied quantitatively, however, by working with cylindrical vessels of equal length but varying diameter. Initial rates for stoichiometric mixtures at 560°C. were found as follows (17):

BULB DIAMETER IN MM.	RATE AT 600 MM.	RATE AT 300 MM.
17	0.85	0.18
32	3.49	0.50
56	9.35	0.94
77	33.8	3.45

These values are roughly proportional to the square of the diameter; the rate at 600 mm. in the largest bulb is about double the expected value, presumably because this measurement was made on the borderline of the high-pressure explosion region.

When a silver reaction vessel is used, this homogeneous reaction is not found (15). There is a slow wall reaction with a rate nearly independent of the hydrogen pressure and unaffected by inert gases. Introduction of a silica rod is without effect. It therefore appears that the reaction chains which leave the silica surface are rapidly destroyed by some action of the silver.

The homogeneous reaction is sensitive to gaseous inhibitors. At 450 mm. and 550°C. the rate is markedly reduced by the addition of 0.01 mm. of chlorine, bromine, or iodine, falling to as little as one-tenth of its original value in the case of iodine (10). When the quantity of halogen is varied, the rate is found to pass through a minimum and then to increase slowly for larger additions, remaining for a long time less than if no halogen were present. There is good evidence that the increase is due to a wall reaction, one step of which is the known heterogeneous oxidation of the hydrogen halide. The actually observed minimum rate, therefore, does not represent the maximum inhibition of the homogeneous reaction. Since the gas reaction is slower in small reaction vessels, it is not surprising that it should be less susceptible to inhibitors; this is found to be the case.

#### THE EXPLOSION REGION

At pressures lower than those of the homogeneous reaction there is a region of more or less instantaneous reaction. This explosion normally takes place only between two well-defined pressure limits, which depend upon the temperature and composition.

Of the two limits, the upper is more easily studied, since the effect there is sufficiently vigorous to be easily noted, and still more since the position of the limit is quite stable. The upper limit is independent of the diameter of the vessel, and is nearly the same in porcelain, silica, and alumina. At constant temperature the limit can be fairly well represented by

$$f_H(H_2) + f_O(O_2) + f_X(X) = \text{const.}$$

where X represents any inert gas and the  $f_H$ ,  $f_O$ ,  $f_X$  are constants. The constant on the right of the equation increases with temperature at a rate corresponding to an activation energy of about 26 kg-cal. (25, 13, 9).

In quartz vessels of moderate size the lower limit is at pressures of the order of 1 mm. (25). In the region near the limit the explosions are feeble and correspondingly difficult to detect. The position of the limit is very susceptible to the pretreatment of the surface, and it is for that reason practically impossible to make really comparable experiments in different vessels. It is at least approximately true, however, that the limit is represented by

$$(H_2)(O_2)d^2 = \text{const.}$$

in the absence of inert gases. In the presence of inert gases the lower limit is lowered, that is, explosion occurs for partial pressures of hydrogen and oxygen which by themselves would be unreactive. The effect of helium is greater than that of argon. It appears to be an unwarranted exaggeration of the experimental accuracy in this difficult region to deduce the functional form of the lower limit taking account of the inert gas effect. The effect of temperature also is rather uncertain. It seems that when the upper and lower limits are far apart, the lower limit decreases only slightly as the temperature is increased, but that for low temperatures, where the two limits come together, the effect is considerably greater.

Within the explosion region ignition is by no means instantaneous. Kowalsky (20) used a photographically recorded membrane manometer to follow the course of the reaction at pressures only moderately above the lower limit. The initial parts of his curves show an exponential increase in rate with time, the acceleration being greater the higher the temperature and the greater the pressure excess over the lower limit. The maximum rates were reached at times of the order of 0.1 sec. This "induction period" is thus quite distinct from the very much longer induction periods characteristic of hydrocarbon-oxygen explosions near the lower limit.

The boundaries of the ignition region are profoundly altered by various departures from the "normal" conditions prevailing in quartz vessels. It has already been suggested that the position of the lower limit is sensitive to the condition of the surface. It is not surprising, therefore, that marked changes are produced when totally different surfaces are used. Thus Frost and Alyea (9), using potassium chloride-coated Pyrex vessels, found the lower limit at pressures some tenfold higher than other workers report in quartz; the dependence of the limit on concentration is also changed, being given by

$$(O_2)[g_H(H_2) + g_O(O_2) + g_X(X)] = \text{const.}$$

The complete absence of surface produces an equally striking effect. Alyea and Haber (1) found by experiments with crossed streams of separately preheated gases that ignition did not occur at 520°C. at pressures of 20–100 mm., well within the ignition region in quartz. The non-igniting gases could be lit by a rod of quartz, glass, porcelain, copper, or iron, but not by one of aluminum. It had previously been shown (12a) that ignition took place with crossed streams at 560°C. and atmospheric pressure.

When an aluminum vessel is used, the ignition is apparently suppressed, but the presence of a quartz rod restores the normal ignition region. With a silver vessel no ignition could be obtained even at 700°C., and in this case the presence of quartz had no effect (15). In fact, it was found that even with a quartz vessel ignition was frequently prevented by the presence

of silver wires; this result was considered ambiguous, however, since the silver wires used, which were apparently more active catalytically than the surface of the silver reaction vessel, produced sufficient steam to quench the explosion.

The addition of a few hundredths of a per cent of nitrogen dioxide produces a very great broadening of the ignition region, the upper limit being raised and the lower limit lowered, and the minimum ignition temperature reduced to about 350°C. (25). For larger additions the limits are narrowed again; as a result, for any fixed mixture and temperature, there are two limiting concentrations of nitrogen dioxide, between which ignition occurs, but beyond which it does not. For constant temperature and composition these limits approach each other as the pressure is raised. For constant pressure and composition they approach as the temperature is lowered. At constant pressure and temperature the upper limit is lowered when the proportion of oxygen is increased, or when nitrogen is added.

Small quantities of halogens affect the ignition in the opposite way, and one part of iodine or bromine in 10,000 suppresses it completely, at least in the normal temperature range. The effect of chlorine is similar but much feebler, 0.25 per cent being required for suppression (10).

Steam has a similar effect, but of quite a different magnitude, 36 per cent being required to suppress explosion as compared with 0.002 per cent of iodine in a similar experiment (10).

A vast number of experiments have been carried out in which reaction in oxygen-hydrogen mixtures is initiated by atoms, by ions, or by molecules in higher quantum states. Tremendous broadening of the ignition region is produced by these additions. The production of active centers by electric discharges passed through the mixture, by means of which explosions can be obtained at room temperature, which is the best-known example of this effect, has been treated in detail in a preceding paper by Bradford and Finch (see page 221). We shall consider here experiments in which atoms are generated by a discharge through one of the gases before mixing. When hydrogen atoms are produced in this way, at a partial pressure of about 0.05 mm., the explosion limits are considerably widened (7), the effect increasing somewhat with the concentration of atomic hydrogen. Atomic oxygen gives a far more striking change, however. With it, ignition of a sort is produced even at room temperature. The upper limit, moreover, either completely disappears or at least recedes beyond the experimental range (22). The different nature of the changes in the limits for the two cases suggests that the addition of atomic hydrogen merely starts more of the normal chains, but that atomic oxygen leads to chains of a new and more fecund kind (17). There are several difficulties in such a view, however, which will be considered later.

Many other experiments deal with ignition or slow reaction due to atoms of hydrogen, oxygen, or chlorine produced photochemically, either directly or by means of photosensitizers such as mercury vapor (23, 19, 21, 3). The most important result of such work is the evidence that slow reaction initiated by either atomic hydrogen or atomic oxygen involves chains which are very short at room temperature, but increase rapidly in length as the temperature nears the ignition region, and that the chief primary product is hydrogen peroxide rather than water.

#### THE REACTION MECHANISM

The general features of the interpretation of these results are the same as have been discussed in the preceding paper on the mechanism of combustion of hydrocarbons. The greater chemical simplicity of the present reaction, however, makes it reasonable to expect the details of the mechanism to be established more completely and more definitely. As yet, unfortunately, this represents more a hope for the future than an accomplishment of the past.

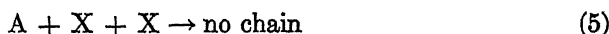
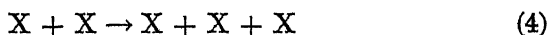
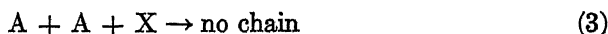
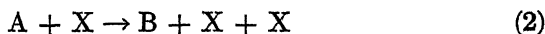
The ignition region is unquestionably due to a chain reaction. The chains ordinarily start on the walls, but a few originate in the gas (1, 12a). Branching occurs in the gas. The chains may be broken either by a triple collision in the gas, or by diffusion to the wall. Ignition takes place, according to the simple theory, when the rate of branching is greater than the rate of breaking. This mechanism gives upper and lower limits to the ignition region. At the upper limit chain breaking is predominantly due to triple collisions. Hence the limit is nearly independent of factors which influence the rate of chain breaking at the walls, that is, of the vessel diameter and of the material and pretreatment of the reaction vessel. Inert gases break chains at triple collisions and hence reduce the upper limit. The lower limit, on the other hand, is determined predominantly by the rate of chain breaking at the walls. It is therefore sensitive to the nature of the walls and to the size of the vessel. Inert gases retard diffusion, and thus lower the lower limit. If no chains start, there can be no ignition, but according to the simple theory any finite rate of starting, however small, is sufficient to give ignition if the net branching rate is greater than zero. In the Alyea-Haber experiment with crossed streams, however, ignition will not be observed unless it develops to a sufficient extent before the crossed streams have been too much weakened by diffusion; in the absence of suitable surface the rate at which chains start in the gas alone does not seem to fulfill this condition below 560°C. Likewise in an aluminum vessel, so few chains start that they do not have time to develop sufficiently before the catalytically formed steam has wiped out the ignition region. When a silica surface also is present, chains start more

rapidly, and ignition occurs. The results in a silver vessel seem to require a different explanation, which will be discussed later.

The effects of sensitizers and inhibitors can be understood in principle as due to their creation of new possibilities for chain branching and chain breaking. A single substance may participate in both processes and thus function in both rôles, as nitrogen dioxide appears to do.

The broadening of the ignition region by artificial creation of chain carriers does not fit easily into the framework of the classical theory. The results with atomic oxygen might be interpreted as representing an entirely new chain, with new limits; the effect of atomic hydrogen, however, is quite obviously a mere broadening of the already existent limits. A possible interpretation is that in addition to the set of branching and breaking reactions involving a single carrier and fixing the normal limits, there are additional branching and breaking reactions involving two carriers in each step, which would, if left to themselves, determine wider limits. For mixtures beyond the normal ignition limits, the first set of reactions alone would determine a steady concentration of chain carriers dependent on the rate of starting chains. If this steady concentration is small enough, it is not appreciably altered by the existence of the second-order reactions. But if the first-order reactions permit the number of chain carriers to increase sufficiently, the second-order set will take command and lead to ignition.

This interpretation may be illustrated by the following very formal example, where normal chain-carrying reactions are omitted, only starting, branching, and breaking steps being shown.



Then

$$dX/dt = k_1A + (k_2A - k_3A^2)X + (k_4 - k_5A)X^2$$

The condition for ignition is that  $dX/dt > 0$  for all values of  $X$ . This condition cannot be fulfilled unless

$$k_4 - k_5A > 0 \quad (I)$$

and also either

$$k_2A - k_3A^2 > 0 \quad (II)$$

or

$$k_1A > (k_2A - k_3A^2)^2/4(k_4 - k_5A) \quad (III)$$

Values of  $A$  for which expression II is not satisfied, but both I and III are, represent broadening of the ignition region. It is evident that the amount of this broadening is greater the greater  $k_1A$  is, that is, the faster chains are being started.

In many experiments, the conditions are better described as a high initial value of  $X$  than by a large value of  $k_1A$ . The condition for ignition in such cases is that  $dX/dt > 0$  for all  $X > X_0$ . If  $k_1A$  can be neglected, which is probably a reasonable approximation under these conditions, ignition will occur if

$$X_0 > (k_3A^2 - k_2A)/(k_4 - k_5A) \quad (\text{IV})$$

Here also, as the initial concentration of chains is increased, the normal limits are progressively widened.

It is obvious that any dependable theory of the lower limit and of the high-pressure gas reaction as well must be based on a sound treatment of the rate of breaking chains at the surface. In many cases it has been thought sufficient to take the surface breaking as equivalent to a volume rate of breaking  $kn/pd^2$ , where  $n$  is the average concentration of chains,  $p$  is a linear function of the various partial pressures, and  $d$  is a linear dimension of the vessel. This treatment can in fact be justified by a consideration of the diffusion equation (5), subject to three conditions: (a) every chain reaching the wall is destroyed; (b) the net rate of branching is proportional to the number of chains in existence; and (c) branching occurs at only a small fraction of all chain-continuing reactions. When the fraction of chains destroyed by a single collision with the walls is a fraction  $\epsilon < 1$ , and conditions b and c are fulfilled, rather different results are obtained (18, 27). In the range  $1 > \epsilon > 0.01$ , the rate of breaking at the wall is scarcely dependent on the value of  $\epsilon$  and the preceding simple rate law is nearly obeyed. As  $\epsilon$  decreases below 0.01, the rate law changes gradually from  $kn/pd^2$  to  $3\epsilon\bar{v}n/2d$ , where  $\bar{v}$  is the mean molecular velocity. In the upper range the rate of breaking is nearly independent of the condition of the surface, and nearly inversely proportional to the diffusion coefficient and to the square of the diameter. In the lower range it is nearly proportional to the chain-breaking efficiency of the surface, nearly independent of the diffusion coefficient, and nearly inversely proportional to the first power of the diameter. When either b or c is not satisfied, special investigation is required. Such an investigation with regard to c appears farther on in this paper.

One of the most puzzling features of this reaction has been the relation between the chain in the ignition region and that in the high-pressure gas reaction. Thompson and Hinshelwood (25) had originally postulated totally different chains in the two regions. This unsatisfying view was

rejected by Grant and Hinshelwood (13), who proposed the following formal theory. Normally the upper limit might be described by



They suggested that if the rôle of M at a triple collision was not to break the original chain but merely to prevent branching, sufficient chains would survive to provide the gas reaction above the upper limit. Kinetic analysis of this theory, however, showed (18) that it predicted totally wrong characteristics both for the gas reaction and for the upper limit, and it seemed necessary to return to the idea of unrelated chains. Very recently, von Elbe and Lewis have found a more plausible interpretation (26). The upper limit is caused by triple collisions



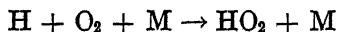
Z is neither a perfectly stable molecule nor a real chain carrier. At the upper limit it is destroyed by diffusion to the walls, but above the limit this diffusion becomes increasingly slow and there is time for Z to regenerate chains by some reaction such as



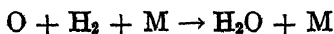
This theory can even account formally for a third isothermal explosion limit, although, as von Elbe and Lewis point out, the actually observed third limit is probably a thermal explosion.

#### SPECIFIC MECHANISMS

The foregoing analysis has provided only skeleton mechanisms. We shall now consider the problem of replacing non-committal X's and Y's with specific intermediates. A systematic treatment of this problem, for the normal ignition limits, was attempted by Kassel and Storch (18), who constructed a catalog of all imaginable reactions involving only a single chain carrier, and investigated the conditions under which the resulting complicated equation for the upper limit would reduce to the correct experimental form. They found two solutions. In one, branching took place at collisions  $H + O_2$ , breaking by



$HO_2$  was not a chain carrier. The second, less plausible, solution involved branching at collisions  $O + H_2$ , and breaking by

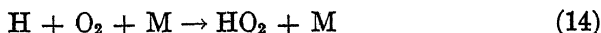




The first solution envisaged the normal chain as (the numbering follows that of Kassel and Storch, with additions as necessary)



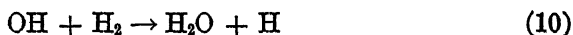
The chains were broken by



The distinction between  $\text{HO}_2$  and  $\text{HO}_2^*$  was that the latter possessed its heat of formation and was an active chain carrier, while the former did not continue the chain. It was necessary for this distinction to be a sharp one, that is, the rate of reaction of  $\text{HO}_2^*$  with  $\text{H}_2$  had to be large compared to its rate of deactivation to  $\text{HO}_2$  by collision with other molecules; if this was not the case, the resulting expression for the upper limit was incorrect. Branching could occur by one or both of



Since all  $\text{HO}_2^*$  reacted with  $\text{H}_2$ , the second of these branching reactions was kinetically equivalent to the first. Branching was completed by



which had to be the only important reaction of  $\text{OH}$ . If reaction 2 was a branching reaction it was necessary to have also



which had to be the only important reaction of  $\text{O}$ .

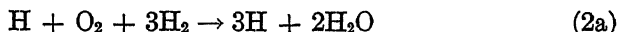
The occurrence of



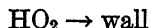
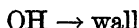
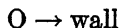
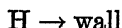
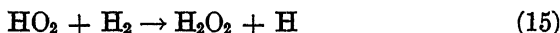
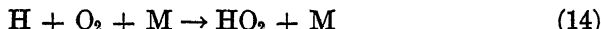
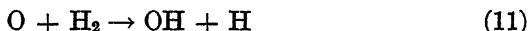
in this mechanism was based on the authors' reluctant acceptance of the Bates and Lavin (2) view that  $\text{HO}_2$  could be formed in a bimolecular association reaction. It is now firmly established by the work of Cook and Bates (6), Farkas and Sachsse (8), and Bodenstein and Schenk (4) that this reaction occurs only at triple collisions. It has been pointed out by von Elbe and Lewis (26) that the mechanism remains unharmed when steps 1, 3, and 5 are deleted. The effectively slow chain step is now



All O and OH formed in reaction 2 react by equations 10 and 11, so that the stoichiometric result of reaction 2 is

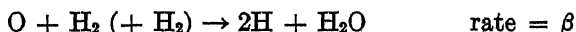


The complete mechanism to account for the ignition region and the high-pressure gas reaction should then be



We shall proceed to a systematic development of the consequences of this mechanism. Since the chain branches at every link, the earlier treatment of the diffusion equation given by Kassel and Storch (18) is not applicable. For an exact treatment it would be necessary to solve four simultaneous diffusion equations. This will not be attempted; instead, various plausible approximations will be investigated separately.

One such approximation which might be applicable at the lower limit is to neglect reactions 14 and 15, and to assume that reaction 10 is very rapid. The kinetic equations for the lower limit are then



The diffusion equations for plane parallel plates are

$$\partial \text{H} / \partial t = D_{\text{H}} (\partial^2 \text{H} / \partial r^2) + 2\beta \text{O} = 0$$

$$\partial \text{O} / \partial t = D_{\text{O}} (\partial^2 \text{O} / \partial r^2) + \alpha \text{H} - \beta \text{O} = 0$$

The most general solution which is permitted by the physical requirements is

$$\text{O} = A \cos (\beta / 2 D_{\text{O}})^{1/2} R_{+} r + B \cos (\beta / 2 D_{\text{O}})^{1/2} R_{-} r$$

$$\begin{aligned} \text{H} = A (\beta / 2 \alpha) (R_{+}^2 + 2) \cos (\beta / 2 D_{\text{O}})^{1/2} R_{+} r \\ + B (\beta / 2 \alpha) (R_{-}^2 + 2) \cos (\beta / 2 D_{\text{O}})^{1/2} R_{-} r \end{aligned}$$

where

$$R_{\pm} = [-1 \pm (1 + 8\alpha D_{\text{O}} / \beta D_{\text{H}})^{1/2}]^{1/2}$$

Equating the net branching rate in the gas to the rate of destruction by the walls gives

$$\begin{aligned} & (\epsilon_0 \bar{v}_0/4) [A \cos (\beta/2D_0)^{\frac{1}{2}} R_+ r_0 + A(\beta/2D_0)^{\frac{1}{2}} R_+ \lambda \sin (\beta/2D_0)^{\frac{1}{2}} R_+ r_0 \\ & \quad + B \cos (\beta/2D_0)^{\frac{1}{2}} R_- r_0 + B(\beta/2D_0)^{\frac{1}{2}} R_- \lambda \sin (\beta/2D_0)^{\frac{1}{2}} R_- r_0] \\ & = AR_+(\beta D_0/2)^{\frac{1}{2}} \sin (\beta/2D_0)^{\frac{1}{2}} R_+ r_0 + BR_-(\beta D_0/2)^{\frac{1}{2}} \sin (\beta/2D_0)^{\frac{1}{2}} R_- r_0 \end{aligned}$$

and

$$\begin{aligned} & (\epsilon_H \bar{v}_H/4) [ - A(\beta/2\alpha) R_-^2 \cos (\beta/2D_0)^{\frac{1}{2}} R_+ r_0 \\ & - A(\beta/\alpha) ( - \alpha/D_H)^{\frac{1}{2}} R_- \lambda \sin (\beta/2D_0)^{\frac{1}{2}} R_+ r_0 - B(\beta/2\alpha) R_+^2 \cos (\beta/2D_0)^{\frac{1}{2}} R_- r_0 \\ & \quad - B(\beta/\alpha) ( - \alpha/D_H)^{\frac{1}{2}} R_+ \lambda \sin (\beta/2D_0)^{\frac{1}{2}} R_- r_0 ] \\ & = (A/R_+)(8\beta D_0)^{\frac{1}{2}} \sin (\beta/2D_0)^{\frac{1}{2}} R_+ r_0 + (B/R_-)(8\beta D_0)^{\frac{1}{2}} \sin (\beta/2D_0)^{\frac{1}{2}} R_- r_0 \end{aligned}$$

These two equations determine  $A/B$  and  $r_0$ . Since no simple explicit solution for  $r_0$  can be found, it is hard to visualize the results. We may, however, investigate a few extreme assumptions.

*Case I.*

$$\epsilon_H = \epsilon_0 = 1$$

Here the solution is simply

$$B = 0$$

$$(\beta/2D_0) R_+^2 r_0^2 = \pi^2/4$$

Since

$$D_0^{-1} = g_H(H_2) + g_O(O_2) + g_X(X)$$

and  $\beta$  is proportional to  $(H_2)$ , this becomes

$$(H_2)[g_H(H_2) + g_O(O_2) + g_X(X)]R_+^2 r_0^2 = \text{const.}$$

The two possible extreme cases are

$$\alpha D_0 \gg \beta D_H \quad R_+^2 = (8\alpha D_0/\beta D_H)^{\frac{1}{2}}$$

and

$$\alpha D_0 \ll \beta D_H \quad R_+^2 = 4\alpha D_0/\beta D_H$$

The corresponding conditions for the lower limit are

$$(H_2)^{\frac{1}{2}}(O_2)^{\frac{1}{2}}[g_H(H_2) + g_O(O_2) + g_X(X)]r_0^2 = \text{const.}$$

and

$$(O_2)[g_H(H_2) + g_O(O_2) + g_X(X)]r_0^2 = \text{const.}$$

The latter of these corresponds in form with the Frost and Alyea expression for the lower limit in potassium chloride on Pyrex.

*Case II.*

$$\epsilon_H = 0 \quad \epsilon_O = 1$$

It is easily seen that for this case the chains branch faster than they can be broken, and there can be no lower limit. This same conclusion can be reached from the general equations, but only after considerable algebra.

*Case III.*

$$\epsilon_H = 1 \quad \epsilon_O = 0$$

For this case also the lower limit is given by

$$(O_2)[g_H(H_2) + g_O(O_2) + g_X(X)]r_0^2 = \text{const.}$$

A far more thorough investigation should be made, but it seems likely that the lower limit data of Frost and Alyea as well as those of Hinshelwood (15) are reconcilable with this mechanism.

The upper limit is treated by neglecting reaction 15 and all wall reactions except the destruction of  $HO_2$ , which is supposed to be fast. The limit is then given by

$$k_{14,H}(H_2) + k_{14,O}(O_2) + k_{14,X}(X) = 2k_2$$

Since there is no reason to expect that the various  $k_{14}$  values have appreciable temperature coefficients, comparison with experimental results requires an activation energy of 24 to 26 kg-cal. for reaction 2. This reaction could then take place at only 1 collision in  $10^7$  at  $550^\circ\text{C}$ . Such a value seems rather small in comparison with the probable rate of triple collision.

For the reaction above the upper limit we restore reaction 15 and take the rate of destruction of  $HO_2$  on the wall as  $k_w(HO_2)/Xd^2$ , a form which is approximately correct when the chains start in the gas and are destroyed at nearly every collision of  $HO_2$  on the wall (27). The rate of starting chains is represented formally by  $S$ . Then

$$\frac{d(H_2O)}{dt} = \frac{2k_2S[k_{15}(H_2)(X)d^2 + k_w] + k_{14}k_{15}(H_2)(X)^2d^2}{k_{14}k_w(X) - 2k_2[k_{15}(H_2)(X)d^2 + k_w]}$$

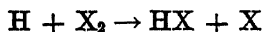
It is possible to show that this equation reproduces at least all the striking qualitative characteristics of the reaction above the limit.

This mechanism thus seems to account for everything to which it is reasonably applicable, *except for the results in silver vessels*. This problem has been discussed fully by von Elbe and Lewis (26). Undoubtedly chains

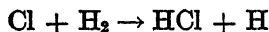
are broken faster in silver vessels than in glass, quartz, or alumina; this cannot be because walls of the latter substances break chains very inefficiently, since in that case the observed lower limit must be inversely proportional to the first power of the diameter and independent of inert gas. These authors have suggested breaking in the gas phase by silver sputtered from the surface by the exothermic reactions occurring there.

Space does not permit any elaborate discussion of the rôle of inhibitors and sensitizers. The mechanism of inhibition by halogens has always been rather clear.

The reactions



are rapid in all cases, and serve to remove chain carriers. The reaction



is also rapid, while the corresponding reactions with bromine and iodine are slow; the relatively weak inhibition by chlorine is thus easily understandable.

The more interesting effects due to addition of nitrogen dioxide have received considerable attention. A mechanism for it has recently been found by von Elbe and Lewis (28) which is consistent with that given above for the non-sensitized reaction, and which will probably stand or fall with the latter.

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# THEORY OF FLAME PROPAGATION<sup>1</sup>

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The purpose of this paper is to discuss the mechanism of the propagation of flame through a combustible mixture relative to the unburnt gas. This rate of flame propagation is sometimes referred to as the fundamental speed of flame or transformation velocity or burning velocity. The considerations will be confined to burning velocities that are far below the velocity of sound, as distinct from detonations that travel with speeds greater than the velocity of sound. The problem of the burning velocity is obviously very complex, the process of flame propagation being dependent on heat flow, on diffusion of many species, particularly active ones such as atoms and radicals, and on kinetics of complex reactions. Therefore at present any theory must necessarily involve hypotheses and approximations.

The study of chemical kinetics is a comparatively recent development. It was natural, therefore, that in the first attempts (10) the problem should have been regarded as one involving primarily the conduction of heat from the burnt to the unburnt gas. To illustrate, let us consider the reaction zone stationary with respect to the coördinate system  $x-T$  in figure 1. The unburnt gas at the temperature  $T_u$  moves in the direction of the arrow against the heat flow along the temperature gradient between the final temperature  $T_b$  (after complete combustion) and  $T_u$ . When its temperature has risen to the ignition temperature  $T_{ig}$ , reaction commences and continues until  $T_b$  is established. Taken as it is, no serious objections could be raised against this picture even today, provided the proper limitation is placed on the interpretation of  $T_{ig}$ . It was widely supposed that

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this temperature was something of the nature of a physical constant of the gas mixture that could be determined in independent experiments. As was perhaps evident in the first section of this symposium on the kinetics of ignition, the ignition temperature is not a physical constant of the gas mixture but is a function of the system as a whole in which ignition occurs and of time (ignition lag). For the case of flame movement it is almost certain that no experiment could be performed that would ensure conditions that simulate those that define  $T_{ig}$ . This is quite apart from the consideration that  $T_{ig}$ , even according to older views of reaction kinetics, would not be a sharply defined temperature but would comprise a certain, possibly small, temperature range within which the reaction becomes so fast that during the further travel of a gas element from  $T_{ig}$  to  $T_b$  the percentage of heat evolution is commensurate with the percentage of distance traveled.

Several attempts have been made to derive an expression for the burning velocity from the foregoing picture. While such derivations cannot lead

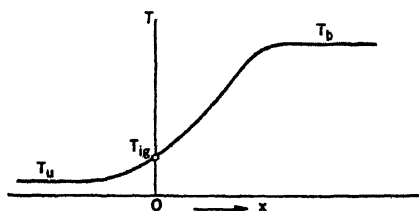


FIG. 1

to a quantitative description, owing to uncertainties in the conception of  $T_{ig}$  and the general lack of knowledge of the reaction rate, they lead to some qualitative conclusions that are not without interest. For this purpose a crude mathematical development will suffice.

The zero point of the  $x$ -axis is placed at the point where the temperature of the gas has risen to  $T_{ig}$ . Consider a stream of combustible mixture of unit area cross section. The unburnt gas at this point is receiving per unit time an amount of thermal energy (required for ignition)

$$H_{ig} = S_u \rho_u \bar{c}_p (T_{ig} - T_u) \quad (1)$$

where  $S_u$  is the burning velocity,  $\rho_u$  the density of the unburnt gas,  $\bar{c}_p$  the average specific heat of the mixture at constant pressure,  $T_{ig}$  the ignition temperature, and  $T_u$  the temperature of the unburnt gas.

Since this heat is transferred by conduction it must be equal to

$$H_{ig} = \mu \left( \frac{dT}{dx} \right)_{x=0} \quad (2)$$

where  $\mu$  is the coefficient of heat conductivity. If it is assumed as a first approximation that  $\left(\frac{dT}{dx}\right)_{x=0}$  is proportional to  $T_b - T_{ig}$ , i.e., the temperature gradient between  $T_b$  and  $T_{ig}$  is substantially linear, then

$$H_{ig} = \mu(T_b - T_{ig}) \frac{1}{x_b} \quad (3)$$

$x_b$  represents the thickness of the reaction zone between  $T_{ig}$  and  $T_b$  and is a function of the reaction rate. It becomes smaller the faster the reaction.

Combining equations 1 and 3 one obtains

$$S_u = \frac{\mu}{\rho_u \bar{c}_p} \frac{T_b - T_{ig}}{T_{ig} - T_u} \frac{1}{x_b} \quad (4)$$

This is substantially the equation originally proposed by Mallard and Le Chatelier (10).

Equation 4 predicts the existence of limits of inflammability. With sufficiently lean or rich mixtures  $T_b$  will decrease, and, although  $T_{ig}$  is presumably a complicated function of mixture composition and other factors, it is evident that  $T_b - T_{ig}$  must vanish while  $T_{ig} - T_u$  remains positive and finite. If in lean mixtures the nitrogen of the air is replaced by oxygen,  $\bar{c}_p$ ,  $\mu$ , and  $T_b$  will not change very much. Neither will the diffusion characteristics of the mixture and the reaction velocity change very much, so that it is not unreasonable to consider  $T_{ig}$  and  $x_b$  substantially unchanged. Thus it can be understood that the lower limit of inflammability is little different in air and in oxygen, as was also pointed out by Jost (5) and as table 1 shows.

For the same reason it is understandable that in sufficiently lean mixtures the substitution of oxygen for nitrogen has little effect on the burning velocity. This is shown in table 2.

If  $T_{ig}$  is reasonably constant over a range of mixture composition near the stoichiometric, the ratio  $\frac{T_b - T_{ig}}{T_{ig} - T_u}$  goes through a maximum for the maximum  $T_b$ ; furthermore,  $x_b$  presumably goes through a minimum at the maximum  $T_b$ . Therefore one can understand the near coincidence of the maximum burning velocity mixture and the maximum flame temperature mixture, both being slightly on the rich side.

The nature of an inert component of the gas mixture will affect principally  $\bar{c}_p$ ,  $\mu$ , and  $T_b$ . If nitrogen is replaced by carbon dioxide, whose specific heat is larger and heat conductivity smaller, the burning velocity should decrease. This is found experimentally (4). If nitrogen is replaced by argon, whose specific heat is much lower, the burning velocity should increase, which is confirmed experimentally (13). Replacing the

argon by helium increases the burning velocity still further (3, 8), which is in qualitative agreement with the larger heat conductivity of helium.<sup>2</sup> The data show, however, that the increase in burning velocity is by no means as large as the increase in the heat conductivity of the mixture. Therefore one would have to postulate a higher  $T_{ig}$  or larger  $x_b$  or both in

TABLE 1

*Lower limits of inflammability of combustibles in air and oxygen under comparable conditions (1)*

COMBUSTIBLE	LOWER LIMIT	
	In air	In oxygen
Hydrogen.....	9.4	9 to 10
Carbon monoxide.....	16.3	16.7
Methane.....	6.1	6.4
Ethylene.....	3.13	3.1
Propylene.....	2.00	2.10
Acetylene.....	3.45	3.1
Diethyl ether.....	1.85	2.10
Divinyl ether.....	1.70	1.85
Cyclopropane.....	2.40	2.45

TABLE 2

*Burning velocities of combustibles in mixtures of oxygen and nitrogen (4)*

MIXTURES	BURNING VELOCITY
	<i>cm. per second</i>
30% of (97.15% CO + 1.5% H <sub>2</sub> + 1.35% H <sub>2</sub> O).....	<div> <div> in (70% N<sub>2</sub> + 30% O<sub>2</sub>)  in (60% N<sub>2</sub> + 40% O<sub>2</sub>)  in (40% N<sub>2</sub> + 60% O<sub>2</sub>)  in (1.5% N<sub>2</sub> + 98.5% O<sub>2</sub>) </div> <div> 31 34 37 39 </div> </div>
30% H <sub>2</sub> .....	<div> <div> in (60% N<sub>2</sub> + 40% O<sub>2</sub>)  in (50% N<sub>2</sub> + 50% O<sub>2</sub>)  in (30% N<sub>2</sub> + 70% O<sub>2</sub>)  in (1.5% N<sub>2</sub> + 98.5% O<sub>2</sub>) </div> <div> 240 250 260 300 </div> </div>
10% CH <sub>4</sub> .....	<div> <div> in (60% N<sub>2</sub> + 40% O<sub>2</sub>)  in (1.5% N<sub>2</sub> + 98.5% O<sub>2</sub>) </div> <div> 60 75 </div> </div>

helium mixtures. This is not unreasonable from kinetic experience, since  $T_{ig}$  would be higher the lower the local concentration of chain carriers, that is, the larger the diffusion coefficient of the mixture. For the same reason the reaction velocity in any layer  $dx$  would be retarded and the

<sup>2</sup> See also Jost (5) for such comparisons.

thickness of the flame front increased. Thus one begins to recognize the importance of diffusion phenomena in the flame front.

Equation 4 can be derived in a different way. The differential equation expressing that in any layer  $dx$  of the stationary reaction zone the rate of change of temperature is zero, is given by

$$\mu \frac{\partial^2 T}{\partial x^2} - \bar{c}_p \rho_u S_u \frac{\partial T}{\partial x} + \frac{\partial H}{\partial t} = 0 \quad (5)$$

The terms in this equation represent the rate of change of thermal energy due to conduction, mass flow, and chemical reaction, respectively. According to the approximation of Mallard and Le Chatelier,  $\frac{\partial T}{\partial x}$  is a constant between 0 and  $x_b$ , and since  $\frac{\partial H}{\partial t} = 0$  for  $x < 0$ , equation 5 is easily integrated to give equation 4.

The Mallard-Le Chatelier equation is sometimes given in another form. The rate of heat liberation for constant  $\frac{\partial T}{\partial x}$  between 0 and  $x_b$  is, from equation 5,

$$\frac{\partial H}{\partial t} = \rho_u S_u \bar{c}_p \frac{(T_b - T_{ig})}{x_b} \quad (6)$$

If  $f$  denotes the reaction rate, defined as the mass of gas that is reacting in the time  $dt$  as the gas passes through the layer  $dx$ , then

$$\frac{\partial H}{\partial t} = f \bar{c}_p (T_b - T_u) \quad (7)$$

Combining equations 6 and 7 and eliminating  $x_b$  in equation 4, one obtains

$$S_u^2 = \frac{\mu}{\rho_u^2 \bar{c}_p} \frac{T_b - T_u}{T_{ig} - T_u} f \quad (8)$$

For the purpose of drawing qualitative conclusions this form has little advantage over the original Mallard and Le Chatelier equation.

Further refinements of the treatment were made by Jouguet (6), Nusselt (11), and Daniell (2). In these treatments the temperature gradient between  $T_b$  and  $T_{ig}$  and the reaction rate were considered to vary along the  $x$ -axis. It will be noted from equation 5 that the assumption of some temperature distribution along the  $x$ -axis automatically fixes the rate of heat liberation, and thus, after introduction of the proper boundary conditions, allows a solution of the problem; this was the procedure chosen by Mallard and Le Chatelier. On the other hand, an assumption concerning the rate of heat liberation along the  $x$ -axis does not alone determine the

temperature distribution. The refinements mentioned consist of introducing some assumption concerning the progress of the reaction along the  $x$ -axis. In order to solve the problem, another equation must be introduced. Since the mass of gas that enters the reaction zone in unit time equals the mass of gas that undergoes chemical reaction within the zone in unit time, this is easily found to be

$$\rho_u S_u = \frac{1}{\bar{c}_p(T_b - T_{ig})} \int_{T_{ig}}^{T_b} \frac{\partial H}{\partial t} \frac{dx}{dT} dT \quad (9)$$

Considering the extreme difficulty of proposing a satisfactory hypothesis concerning the progress of the reaction along the  $x$ -axis, it is evident that these investigations could not have led any further than the Mallard-Le Chatelier treatment. Little has been gained by these attempts beyond a more fully developed mathematical formalism. The incorporation of the cooling effect of the walls in Daniell's treatment of the propagation of flame in tubes may be noted, which demonstrates the existence of a lower critical diameter below which propagation is impossible.

The weakness in all of the above treatments is the concept of ignition temperature as a true physical constant of the gas mixture. In any attempt to develop the theory beyond the stage in which it was left by Mallard and Le Chatelier, it would seem appropriate also to eliminate ignition temperature as an assumed given quantity. In view of the development of reaction kinetics, one must assume that the layer in the unburnt gas in which the reaction becomes fast will be determined not only by a temperature condition but to a large degree by the concentration of active particles or chain carriers. The reaction zone itself may be considered to be abnormally rich in active particles which must diffuse in both directions, toward the burnt and the unburnt gases. The combined effect of diffusion of active particles and heat flow will carry the reaction zone forward into the unburnt gas. It is at once evident that the problem has become considerably more complicated, and it is only by daring approximations that a solution along these lines is at all possible.

One may leave the problem thus unsolved mathematically or attempt a solution with the introduction of approximations. It has, however, become sufficiently clear that diffusion plays an important rôle in the propagation of flame and that this diffusion concerns the migration of chain carriers into the unburnt gas where it renders the latter reactive. A solution has been attempted here, and the results will be given for a particular case.

In order to overcome the difficulties inherent in the simultaneous treatment of heat conduction and diffusion, Lewis and von Elbe (9) proposed the following hypothesis. The sum of thermal and chemical energy per unit

mass in any layer  $dx$  between the unburnt and burnt gases is sensibly constant. To consider the consequences of this hypothesis, it will be noted that the chemical energy in the unburnt gas at the temperature  $T_u$  is equal to the thermal energy needed to raise the temperature of the burnt gas from  $T_u$  to  $T_b$ , neglecting the generally inappreciable loss due to radiation. Any layer of gas between the unburnt and burnt gases if allowed to complete its reaction adiabatically would acquire a temperature  $T_b$ . The hypothesis may be understood to be based on the following considerations. Since thermal energy flows from the burnt to the unburnt side and chemical energy predominantly in the opposite direction, there is a tendency to equalize deviations from the average total energy content. There will, of course, be an excess of energy in the unburnt gas, formerly denoted by  $H_u$ ; this energy "hump" is conceivably much smaller than would correspond to earlier ideas concerning ignition temperature values. The latter may be very low, owing to the presence of active particles which, of course, represent a form of chemical energy imparted to the unburnt gas in excess of its original chemical energy content. However, owing to the property of active particles to promote a reaction efficiently, this excess energy is conceivably very small and the energy hump on the unburnt side is therefore flat.

This hypothesis allows one to confine the analysis to the flow of chemical energy which is transported through the reaction zone by mass flow. Lewis and von Elbe have attempted to develop a theory of the propagation of flames traveling through ozone-oxygen mixtures, the decomposition of ozone being a reaction of comparative simplicity. The overall reaction



is presumed to proceed by the following steps:



where  $\text{O}_2^*$  is an energy-rich molecule. One should also take into consideration the reaction



It will be necessary to simplify this mechanism further. It will be assumed that both reactions b and c proceed fast compared to reaction a, so that thermodynamic equilibrium between O and  $\text{O}_3$  is sensibly established in any layer. This assumption will be in error, particularly on the unburnt side where the concentration of oxygen atoms which have arrived by diffusion will exceed the equilibrium concentration. At higher temperatures, that is, toward the burnt side, it is quite possible that the assumption is not

very much in error. Therefore, we shall consider the mechanism to consist only of reaction a and reaction d,



Denoting by  $N_{\text{O}}$ ,  $N_{\text{O}_2}$ , etc. the number per cubic centimeter of the atoms or molecules indicated by the subscripts, the relation

$$\frac{N_{\text{O}} N_{\text{O}_2}}{N_{\text{O}_3}} = K \quad (10)$$

is thus assumed to hold in any elementary layer  $dx$ .  $K$  is the equilibrium constant and is a function of temperature. According to published data (7)

$$K = 3.03 \times 10^9 \frac{N_{\text{O}_2(b)}}{P} \frac{T_b}{T} e^{-12,800/T} \quad (11)$$

where  $P$  is the pressure in millimeters of mercury and  $N_{\text{O}_2(b)}$  is the number of molecules in 1 cc. at the end of the reaction zone, namely where the temperature is  $T_b$ .

The hypothesis that the sum of thermal and chemical energy per unit mass is constant in any layer within the reaction zone may be expressed by the equation

$$N_{\text{O}_3} E_{\text{O}_3(T)} + N_{\text{O}} E_{\text{O}(T)} = (N_{\text{O}_2} + 1.5 N_{\text{O}_3} + 0.5 N_{\text{O}}) C_{p,T}^{T_b} (T_b - T) \quad (12)$$

where  $E_{\text{O}_3(T)}$  is the heat of decomposition of 1 mole of ozone at the temperature  $T$ ;  $E_{\text{O}(T)}$  is the heat of recombination of 1 mole of oxygen atoms at the temperature  $T$  and is approximately equal to 59,000 cal.;  $C_{p,T}^{T_b}$  is the mean molar heat capacity of oxygen at constant pressure between the temperatures indicated.

Since the burning velocity is small compared to sound velocity, the pressure will be practically constant throughout the reaction zone, and one obtains from the gas law

$$N_{\text{O}_2} + N_{\text{O}_3} + N_{\text{O}} = N_{\text{O}_2(b)} \frac{T_b}{T} \quad (13)$$

Since the mixtures whose experimental burning velocities will be compared with the theory contain considerably more oxygen than ozone, no serious error is introduced by the approximation

$$N_{\text{O}_2} \simeq N_{\text{O}_2(b)} \frac{T_b}{T} \quad (14)$$

This approximation is particularly allowable at intermediate and higher temperatures because the concentrations of  $\text{O}_3$  and  $\text{O}$  that are required to fulfill equation 12 become very small.

From the concentration of  $O_2$  in any layer, the concentrations of  $O_3$  and  $O$  and the temperature  $T$  in the layer are determined by the foregoing system of equations. The condition for the stationary state is now simply that the rate of change of concentration of  $O_2$  in any layer due to diffusion, mass flow, and chemical reaction is zero. This leads to

$$D \frac{\partial^2 N_{O_2}}{\partial x^2} - \frac{\partial}{\partial x} (N_{O_2} S_x) + \left( \frac{\partial N_{O_2}}{\partial t} \right)_c = 0 \quad (15)$$

$D$  is the diffusion coefficient. Since the  $O_2$  concentration decreases with increasing temperature (equation 14) and the positive direction of the  $x$ -axis is the direction of increasing temperature, the sign of the diffusion term is positive.  $S_x$  is the flow velocity through any layer  $x$ . Since the percentage of  $O_2$  in the mixture increases in the direction of unburnt to burnt gas, more oxygen molecules are pushed out of the layer  $dx$  than are pushed in by mass flow. The second term is therefore negative. The third term is the rate of formation of oxygen molecules by chemical reaction.

$S_x$  can also be interpreted to mean the volume of gas passing unit area per second. Since all volumes  $S_x$  contain equal masses, then from the gas law and the increased number of moles due to reaction

$$S_x = S_u \frac{T}{T_u} \frac{1 + 0.5a + m}{1 + m} \quad (16)$$

where  $m$  is the ratio of moles of  $O_2$  to moles of  $O_3$  in the original mixture, and  $0 \leq a \leq 1$ . However, in conformity with the approximations made in equation 14, it is essentially correct, especially for intermediate and higher temperatures, to write

$$S_x = S_u \frac{T}{T_u} \quad (17)$$

The diffusion coefficient is given by

$$D = \frac{\bar{v}\lambda}{3} \quad (18)$$

where  $\bar{v}$  is the average molecular velocity and  $\lambda$  the mean free path. For this purpose the gas may be considered to consist entirely of oxygen molecules. Using numerical values (14)

$$D = 2.2 \times 10^{-2} \frac{T^{3/2}}{P} \quad (19)$$



The rate of formation of  $O_2$  by the chemical reaction is given by the number of successful collisions between  $O$  and  $O_3$  per second per cubic centimeter, viz.,

$$\left(\frac{\partial N_{O_2}}{\partial t}\right)_c = 2Ze^{-E/RT} \quad (20)$$

where  $Z$  is the collision frequency which is given by

$$Z = 2N_O N_{O_3} \sigma_{O,O_3}^2 \left(2\pi RT \frac{M_O + M_{O_3}}{M_O M_{O_3}}\right)^{1/2} \quad (21)$$

where  $M_O$  and  $M_{O_3}$  are the molecular weights of  $O$  and  $O_3$ .  $E$  is the energy of activation, the best available value being about 6000 cal. per mole (12, 15).

TABLE 3

*Comparison of calculated and experimental burning velocities of ozone-oxygen mixtures*

<i>P</i> <i>mm. Hg</i>	<i>T<sub>u</sub></i> °K.	<i>T<sub>b</sub></i> °K.	<i>m</i>	<i>S<sub>u</sub></i>	
				Experimental <i>cm. per second</i>	Calculated <i>cm. per second</i>
624	300	1239	3.054	55	253
2560	427	1343	3.054	158	451
595	302	1922	1.016	160	333
3760	468	2044	1.016	747	664

It will be recalled that in equation 5 the choice of a function for  $\frac{\partial H}{\partial t}$  did not suffice to arrive at a solution until equation 9 was introduced. Similarly, in the present case, it is necessary to introduce an equation analogous to equation 9, which may be written

$$S_u N_{O_3(u)} = \frac{1}{1.5} \int_{T_u}^{T_b} \left(\frac{\partial N_{O_2}}{\partial t}\right)_c \frac{dx}{dT} dT \quad (22)$$

where  $N_{O_3(u)}$  is the concentration of  $O_3$  in the unburnt gas. All equations necessary for the solution of the problem have now been given.

The mathematical development of the equations was carried out by Lewis and von Elbe (9) and calculations of burning velocities were made for certain mixtures for which experimental values were available. The results are given in table 3.

An agreement exists in the order of magnitude, which, considering the assumptions that had to be introduced, would not seem to be unsatisfactory. This indicates that an analysis of the structure of the

reaction zone by the foregoing theory would also lead to agreement in the order of magnitude in the temperature and concentration gradients. Such an analysis is given in figure 2. It is seen that the thickness of the flame front is of the order of  $10^{-3}$  to  $10^{-4}$  cm. The distributions of the reaction rate and of the concentration of the chain carriers (oxygen atoms) are of interest. The latter are seen to reach a high local concentration in a zone of a thickness of the order of one hundred mean free paths. One may perhaps generalize this result by stating that high concentrations of chain carriers are needed in order to produce the fast chemical reaction required for the propagation of flames.

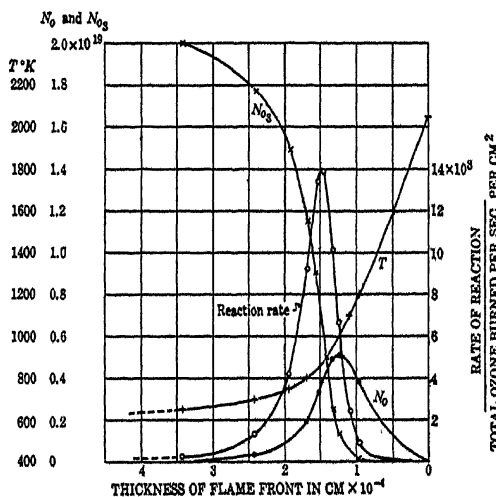


FIG. 2. Structure of reaction zone of ozone flame, showing temperature gradient, distribution of ozone and oxygen atoms, and the reaction rate throughout the zone. 49.6 per cent ozone in oxygen; pressure = 3760 mm. Hg;  $T_u = 468^\circ\text{K}$ ;  $T_b = 2044^\circ\text{K}$ .

Substances that accelerate or retard chemical reaction must also exert a similar influence on the burning velocity. The area under the rate curve in figure 2 would be either increased or decreased. Since the activation energy is of less importance at high temperatures, one may suggest that the increase or decrease of the area occurs mainly on the low-temperature side of the rate curve.

#### SUMMARY

In Mallard and Le Chatelier's treatment of flame propagation the problem is considered simply one of heat flow in which the unburnt gas is raised to its ignition temperature. Although crude, this treatment is able to explain a number of observations: limits of inflammability, effect of

diluent gases on the latter and on rate of flame propagation, and near coincidence of maximum flame temperature mixture and maximum speed mixture. Later elaborations of Mallard and Le Chatelier's treatment have not advanced the problem appreciably, owing to the indefiniteness of the term "ignition temperature." Certain observations show the importance of diffusion in the treatment of flame propagation. A solution of the problem without the use of ignition temperature has been attempted for the propagation of ozone-oxygen flames, using simplifying assumptions concerning the reaction mechanism and the combined effects of heat flow and diffusion. Agreement in the order of magnitude is found between calculated flame speeds and experimental values. In the flame front there is a steep temperature gradient and also a high local concentration of active species. The width of the flame front is calculated to be of the order of  $10^{-3}$  cm. Some consideration is given to the effect of activators and inhibitors on flame speed.

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## PROBLEMS IN FLAME PROPAGATION

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We suggest that the outstanding problem in flame propagation is to ascertain the mechanism by which flame travels through an inflammable gas mixture, i.e., to correlate the speed of movement of flame with the various chemical and physical factors involved by means of an equation with no empirical constant. It may be expected that when this has been accomplished the solution of most of the other problems in flame propagation will follow immediately or will have been found incidentally. Such a correlation has been made for detonation in gaseous mixtures, on the theory that in this mode of burning the zone of reaction is propagated by a mechanical shock wave maintained by the chemical reaction. In this communication we propose, therefore, to consider only the more usual mode of propagation, in which the pressure of the gas in the flame is not sensibly greater than that of the rest of the gas.

### OBSERVED SPEEDS OF FLAME

At comparatively low rates the speed of flame relative to an observer is a function of three factors: (a) the movement of the medium in which the flame is travelling, (b) the area of flame relative to the area of cross section of gaseous mixture to which it is exposed, and (c) the speed of flame relative to the gas mixture itself. It has been shown that the observed speed of flame in a moving medium, whose motion may be imposed from without or may be caused by the expansion due to the heat of the flame itself (13), is equal to the speed in a still mixture plus the speed of movement of the medium (5), and also that the amount of mixture burned is proportional to the area of flame in it (11, 6).

The fundamental speed of flame (c) is the linear speed of the flame, in a direction at right angles to its surface, through a mixture at rest and at constant temperature and pressure just ahead of the flame. The observed speed of flame travelling in a tube is, therefore,

$$\text{Fundamental speed} \times \frac{\text{area of flame}}{\text{area of cross section of tube}} + \text{speed of movement of medium}$$

At higher speeds, during what has been termed the predetonation period, compression factors, which attain their maximum effect in detonation, may also exert a pronounced influence (17).

#### FUNDAMENTAL SPEED OF FLAME

The conception just defined as the fundamental speed of flame may be what Mallard and Le Chatelier (13) had in mind when they wrote of "*la vitesse normale*," which was characteristic of "deflagration" (as distinct from detonation) and was, they thought, observable in the propagation of flames, not accelerated by turbulence or by expansion of the burning gases, in tubes wide enough to eliminate the effect of cooling by the walls of the tubes. The term of Mallard and Le Chatelier is as ambiguous in French as in English, we have been informed, in that the word "*normale*" may mean either "ordinary" or "at right angles to its surface." The term "fundamental" is suggested as preferable (6).

The fundamental speed of flame is the most difficult of all factors to analyze, the others, as has just been shown, being of an obvious mechanical nature. The mode of transfer of energy from the flame front to the neighboring unburnt layers remains to be established, and when physico-chemical hypotheses on this process are formulated, they must be tested by measurements of the fundamental speed. What measurements of this are available?

#### MEASUREMENTS OF THE FUNDAMENTAL SPEED OF FLAME

Le Chatelier's attempt to determine the "*vitesse normale*" from measurements of the speed of flame in tubes was based on the assumption that the flame front was plane and normal to the axis of the tube; the attempt failed because, as was shown later, the flame front is strongly curved (4). Three methods have subsequently been used with success. They may be called (a) the Bunsen cone method, (b) the soap-bubble method, and (c) the method based on measurements of the shape of the flame front and its speed of translation during the uniform movement of flame in a tube.

From the dimensions of the inner cone of a Bunsen flame, burning a known mixture at a known rate, can be calculated the component of the linear speed at which the mixture meets the stationary flame, normal to its surface (11). This is reasonably assumed to be equal to the speed of flame in a stationary mixture, but experimental difficulties make some of the results unreliable; for example, flame speeds have been deduced by this method for mixtures containing from 14 to 17 per cent of methane, although these mixtures do not propagate flame, and mixtures containing less than about 7.3 per cent of methane do not burn on the Bunsen burner, although the lower limit of inflammability of methane is about 5 per cent.

These errors are due to the entrainment of air at the orifice of the burner. The measurements of speeds of the more explosive mixtures, containing from 8 to 12 per cent of methane, may be made fairly reliable by careful attention to experimental conditions (6).

The soap-bubble method, first used by Stevens (19), depends on measurement of the speed of a spherical flame front travelling in a medium which is put in motion by the flame. From this measurement is deduced the speed in a stationary mixture, on the assumption that the observed speed is equal to the fundamental speed plus the speed of movement of the medium due to thermal expansion. This method is applicable to mixtures which burn at a sufficient rate to make negligible the effects of convection. Its results agree with those of the Bunsen flame method, so far as experiments have been made with the same mixtures (20).

The third method is more laborious than the others, and requires more special apparatus. Its results are claimed to be more accurate for the only mixtures to which it has been applied, namely, those of methane and air (6).

It seems clear that all three methods of measurement lead to the same constant, the fundamental speed of flame, and that one or another method is preferable, according to the nature of the flame. The first is simplest, but reliable only with mixtures of composition near to that of the mixture for complete combustion; the second is successful only with fast burning mixtures; the third is the only accurate method for slow burning mixtures.

#### THEORETICAL ANALYSIS OF FUNDAMENTAL SPEEDS

Mallard and Le Chatelier regarded the "vitesse normale" (fundamental speed) as governed by the transfer of heat by conduction from the flame to the nearest unburnt layer of gas, and deduced the formula:

$$v = \text{const.} \cdot \frac{k}{c} \cdot \frac{T_f - T_i}{T_i - T_0}$$

in which  $k$  = thermal conductivity,

$c$  = mean specific heat,

$T_f$  = temperature of the flame,

$T_i$  = ignition temperature, and

$T_0$  = temperature of the unburnt mixture at some distance from the flame.

Crussard (8) gave a modified formula, introducing the rate of chemical reaction as a factor:

$$v = \sqrt{kF \frac{v_0}{c} \cdot \frac{T_0}{T_i} \cdot \frac{T_f - T_i}{T_i - T_0}}$$

in which  $F$  = rate of reaction and  $v_0$  = initial specific volume.

Nusselt (15) gave a somewhat similar formula, but the factor for reaction rate was represented by the concentrations of the reactants. For mixtures of hydrogen and air his equation was

$$v = \text{const.} \sqrt{k \cdot \frac{p_0 T_0^2}{c} \cdot \frac{T_f - T_i}{T_i - T_0} \cdot [\text{H}_2][\text{O}_2]}$$

in which  $p_0$  = pressure and  $[\text{H}_2]$ ,  $[\text{O}_2]$  are the concentrations of hydrogen and oxygen.

Daniell (9) gave the formula

$$v = \sqrt{kF \cdot \frac{v_0}{c} \cdot \frac{T_0}{T_m} \cdot \frac{T_f - T_0}{T_i - T_0}}$$

in which  $T_m$  is a (harmonic) mean temperature which is probably nearer to  $T_f$  than to  $T_i$ .

All the foregoing formulas are based on the theory that flame is propagated by conduction of heat (except in the detonation wave) and all contain the independent variable  $k$ , the thermal conductivity of the mixture, either as  $k$  or  $\sqrt{k}$ . Their validity can readily be tested, for it is easy to prepare series of mixtures which differ greatly in thermal conductivity and very little in any other property which affects the speed of flame. Such mixtures are those of an inflammable mixture with two or more of the inert gases, severally, in the same ratio. The speeds of uniform movement of flame in a series of mixtures of methane and atmospheres approximately  $\text{O}_2 + 4\text{A}$  and  $\text{O}_2 + 4\text{He}$  were measured some time ago; in mixtures of equal percentages of methane, the speeds with the helium atmospheres were somewhat higher than with the argon atmospheres, but not nearly in proportion to the thermal conductivities of the mixtures (7). Some hitherto unpublished observations of a similar character, in which the inflammable gas is hydrogen, are shown in figure 1 (12). Moreover, the various mixtures of hydrogen and oxygen propagate flame at speeds which are nearly equal for each pair of mixtures  $2\text{H}_2 + \text{O}_2 + n(\text{H}_2 \text{ or } \text{O}_2)$ , in spite of the great difference in thermal conductivity according as the one gas or the other is in excess (figure 2, drawn from results in reference 3).

The comparative measurements just quoted were made on the uniform movement of flame. This is an imperfect basis for comparison unless the areas of the flames are equal, because if, for example, the area of one were  $n$  times the area of the other and the speeds of uniform movement were equal, the fundamental speed of the first would be but  $1/n$  of that of the other. A series of comparative experiments in which the fundamental speeds of flame were measured has therefore been made (12), the results of which are shown in table 1.

Although the thermal conductivities of these mixtures at flame temperatures have not been measured, it must surely be that their ratio, or even the square root of their ratio, is much higher than the ratio of the funda-

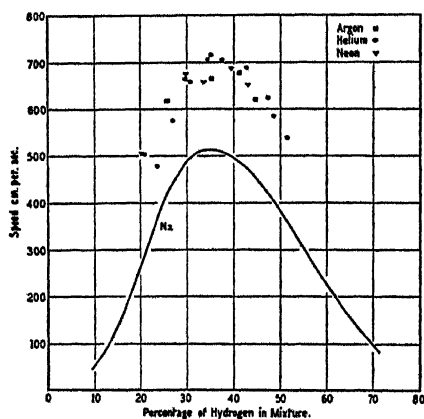


FIG. 1

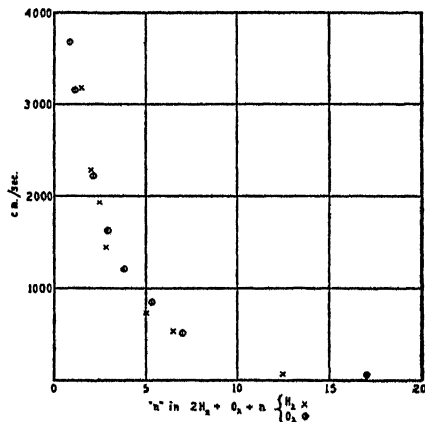


FIG. 2

FIG. 1. Speed of uniform movement of flame in mixtures of hydrogen with air (curve  $N_2$ ) or air in which the nitrogen was replaced by an equal volume of argon or neon or helium. Observations in a tube having a diameter of 2.5 cm.

FIG. 2. Speed of uniform movement of flame in mixtures of hydrogen and oxygen. Observations in a tube having a diameter of 2.5 cm.

TABLE 1

*Speed of flame in a tube, 2.5 cm. in diameter, in mixtures of 10 per cent of methane with 90 per cent of an atmosphere containing argon or helium*

COMPOSITION OF ATMOSPHERE	SHAPE OF FLAME FRONT	SPEED OF UNIFORM MOVEMENT	AREA OF FLAME FRONT	FUNDAMENTAL SPEED OF FLAME
per cent		cm. per second	cm. <sup>2</sup>	cm. per second
Oxygen:20.9 Helium:79.1} .....	Symmetrical	206	12.3	82
Oxygen:20.9 Argon: 79.1} .....	Symmetrical	138	11.4	59

mental speeds of flame. Hence the speed of propagation of flame is not correctly expressed by any of the formulas quoted.

The conclusion just reached does not mean that the propagation of flame is not governed by conduction of heat from the burning to the neighboring unburnt layer, for the slow factor in the succession of events



may be the chemical reaction itself, and the speed of flame may measure mainly the speed of chemical reaction. Without making any attempt at finality we may now refer briefly to some of the outstanding experimental observations that must guide future theoretical developments.

1. The calorific value of the mixture mainly determines the relative speed of flame in a series of mixtures, in various proportions, of the same constituents. Figure 2 shows this; dilution of the mixture  $2\text{H}_2 + \text{O}_2$  with equal quantities of hydrogen or oxygen caused the same reduction in the speed of "uniform movement" of flame.

The speeds of flame in a series of mixtures of various combustible gases, individually, and air reach a maximum at a composition somewhat on the rich side of the mixture of maximum calorific value. The displacement has been interpreted as an effect of mass action (16).

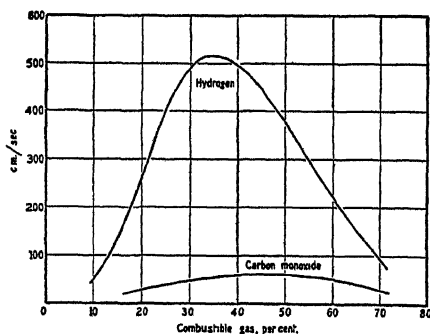


Fig. 3. Speed of uniform movement of flame in mixtures of hydrogen and air, and of carbon monoxide and air. Observations in a tube having a diameter of 2.5 cm.

2. The speeds of flame in various mixtures of equal calorific value may be greatly different; for example, the speeds of uniform movement of flame in mixtures of hydrogen and air on the one hand and carbon monoxide and air on the other, which are shown in figure 3. The differences are too great to be due to differences in thermal conductivity, and must be explained by differences in the rates of reaction or in the production of active radicals, or both.

3. Ignition temperatures, corresponding with the very short lags (in time) available in the propagation of flame, have not been determined except perhaps for mixtures of methane and air. It is, therefore, not yet possible to correlate ignition temperatures with the speeds of flame, but in any case an ignition temperature is a function of simpler properties, and so any connection discovered between ignition temperature and flame speed would only be one step towards a final solution of the problem.

4. The propagation of flame is obviously a continuous succession of ignitions of unburnt gas next to the flame front. It might therefore be expected that the most easily ignited mixtures would be those which would propagate flame most rapidly. This is not so, as the following table will show.

Mixture in which the speed of flame is a maximum.....	10 per cent methane
Most readily ignited mixture	by heated silica surface..... 5 to 6 per cent (14)
	by adiabatic compression..... 7 to 7.5 per cent (10)
	by impulsive electric spark..... 8.2 to 8.3 per cent (21)
	by the detonation of a solid explosive. 8.7 to 9.3 per cent (18)

5. The relative rates of isothermal reaction of a series of mixtures at temperatures below those of ignition are not parallel to the speeds of flame in the same mixtures. Thus at 250–400°C. the most reactive mixtures of each of the simple paraffin hydrocarbons with oxygen are those containing hydrocarbon and oxygen in the molecular proportion 2:1 (2). Far from these mixtures giving the maximum speed of flame, none of them, at room temperature, can propagate flame.

6. There is evidence that, with hydrocarbons, the course of the chemical reactions is the same in flames as at lower temperatures (2, 1), but there exist various rival theories of these and other oxidations.

7. Of much significance is the smallness of the effect of large differences in thermal conductivity on the speed of certain flames, other conditions being the same. There must be a less steep temperature gradient in front of the flame in the mixtures of higher thermal conductivity, and preflame reaction must start correspondingly sooner. But the layer of gas just in front of the flame does not ignite any sooner. What is it waiting for? The indication is that the "bursting into flame" is a consequence of the arrival not so much of sufficient heat as of a sufficient concentration of active particles which, provided that they do not lose their activity to or share it with the inert gas, would diffuse at equal rates from the flame front of such mixtures as we are comparing (combustible + oxygen + argon or helium), whereas the diffusion rate of the heat would be different. Hence the active particles owe their efficiency, as propagators of flame, to their chemical nature rather than to their kinetic energy. The conclusion is, therefore, that they belong to some species of radical or atom.

If, however, such an interpretation is to be given to the equality of flame speeds for each pair of mixtures with equal values of  $n$  in the series  $2\text{H}_2 + \text{O}_2 + n\text{H}_2$  and  $2\text{H}_2 + \text{O}_2 + n\text{O}_2$  (figure 2), then the concentration of active particles must be the same in each pair, whether the hydrogen or the oxygen be in excess. More direct evidence that this is so is to be sought.

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# THE MEASUREMENT OF FLAME SPEEDS<sup>1</sup>

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## INTRODUCTION

When an explosive mixture of gases is ignited by a spark from within, flame spreads in all directions from the point of ignition. The observed spatial velocity of the flame front in any direction is always the resultant of two component velocities,—(1) the speed of propagation relative to the unburned gases, and (2) the speed at which the flame front is transported bodily in a direction normal to its surface by mass movement of the gases comprising it. The first component, or the speed at which the reaction zone advances into and transforms the unburned charge, is a characteristic property of the explosive mixture. This property, which for brevity will be termed the “transformation velocity,” has considerable practical and theoretical importance. The second component or “gas velocity” and the resultant speed in space are of minor fundamental interest, since they vary with the size and shape of the explosion vessel and are influenced by general movements initially present in the gaseous charge or established during combustion.

Unfortunately, very few of the many available records of the spatial movement of flame in bombs, tubes, and engines can be analyzed to yield accurate values of transformation velocity. Reliable experimental data showing the separate effects of the various operating factors upon this fundamental flame speed are extremely scarce. Moreover, the micro-mechanism of flame propagation is still so obscure that there is no adequate basis for calculating transformation velocities from theoretical considerations.

There is need for a clear general picture on a molecular scale of the structure of flame and its mode of propagation which will permit visualization of the effects upon flame speeds of such basic factors as the pressure, temperature, composition and turbulence of the explosive mixture. Ac-

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curate experimental values of transformation velocity would be of great assistance in the evolution of a satisfactory theory of flame propagation and are essential to the verification of any such theory.

In the engine, the rate of rise in pressure is largely determined by the transformation velocity of the explosive mixture used. Complete information regarding the effects of composition, temperature, pressure, and turbulence upon this velocity would be of immediate practical value in predicting and controlling rates of pressure rise. Such data, if extended to sufficiently high temperatures and pressures, should also indicate the conditions for incipient fuel knock. Under these conditions high transformation velocities are to be expected, and autoignition of the unburned charge is probably imminent.

For the reasons which have been enumerated, a primary requisite of a satisfactory method for measuring flame speeds is that it must yield reliable values of transformation velocity. Capacity to function properly over a wide range of operating conditions is a decided advantage. The possibility of obtaining simultaneous information on expansion ratio, heat capacity, equilibrium state, or other factors which influence the amount and rate of the rise in pressure should not be overlooked.

Transformation velocities have been measured for stationary flames and flames moving in tubes and bombs of various shapes. The problems of the stationary flame are discussed by another author (6). It is believed that those methods involving spherical flames are susceptible of the most rigorous analysis.

In the present report, both constant-pressure and constant-volume methods involving spherical flames in the absence of detonation are discussed. Applications of these methods are presented and typical results are given to illustrate some of their salient features. The material of this report has been accumulated during the course of investigations sponsored by the National Advisory Committee for Aeronautics.

#### CONSTANT-PRESSURE EXPLOSIONS

One of the simplest methods yet devised for determining transformation velocity is the soap-bubble or constant-pressure method developed by F. W. Stevens. This method has been described (7) and early results obtained by its use have been fully reported before the American Chemical Society (7, 8, 9) and elsewhere (11, 12). A further investigation of the method by Fiock and Roeder (2) led to a number of refinements in the apparatus and procedure which improved considerably the accuracy of the results obtained and indicated more fully the possibilities and limitations of the method.

*Experimental method*

In the improved procedure, a soap bubble, shown in figure 1, is blown by introducing a carefully prepared explosive mixture through the glass tube seen at the top of the photograph. The ring of gold wire just below the mouth of the tube helps to support the bubble, which is blown until its horizontal diameter becomes 9 cm., as shown by its projected shadow on an enlarged scale. The electrodes, projecting upward from the bottom, form a spark gap at the center of the full-sized bubble, which may be blown without difficulty with the gap in position.

High-speed motion pictures, reproduced in figure 2, show that when the spark occurs, a sphere of flame forms at the spark gap and grows steadily in size until all of the explosive mixture is inflamed. During its growth, the

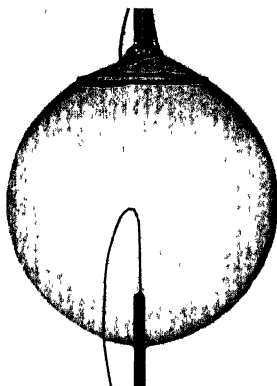


FIG. 1. Soap bubble containing explosive mixture, ready to be fired

flame maintains a spherical shape except for slight local distortions at the supporting ring and the electrodes. The soap film at first distends, then bursts when the flame reaches the gold ring, and finally collapses toward the electrodes without offering appreciable resistance to the progress of the flame. The explosion thus runs its course at constant pressure. There is no measurable convective rise of the sphere of flame during the period of spread except for very slow-burning mixtures. However, the hot gases subsequently rise out of the picture before they cease to glow.

For analytical purposes, the explosion in the bubble is photographed through a narrow slit which leaves only the horizontal diameter visible. The film is carried on a drum rotating at a known constant speed on an axis parallel to the slit. As the diameter of the sphere of flame increases, its lengthening image moves along the film and produces a V-shaped trace

which is a time-displacement record of the travel of the flame front. A typical record is shown in figure 3.

For most mixtures the sides of the V are practically straight, showing that the flame front travels at constant speed. This speed in space ( $S_s$ )

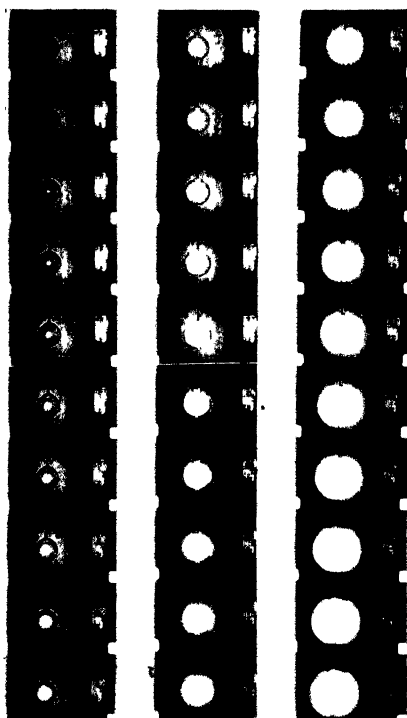


FIG. 2

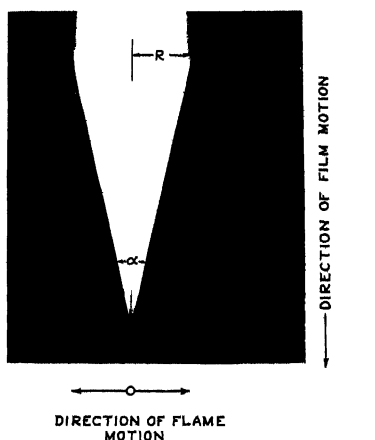


FIG. 3

FIG. 2. High-speed motion-picture record of an explosion in a soap bubble (1610 frames per second)

FIG. 3. Method of recording an explosion in a bubble on a rotating film

can be calculated from the angle ( $\alpha$ ) of the V, the known speed ( $F$ ) of the film, and the magnification factor ( $m$ ) for the camera, through the relation

$$S_s = mF \tan \frac{\alpha}{2} \quad (1)$$

Measurements on the film also show that the final diameter of the sphere of hot gases is much greater than the diameter of the original bubble. The ratio of the volume of the burned products to that of the unburned charge is the expansion ratio  $E$  for the mixture when burned at constant

pressure. If  $r$  is the radius of the bubble before firing and  $R$  is the maximum radius of the sphere of hot gases as measured on the film, then

$$E = \frac{(mR)^3}{r^3} \quad (2)$$

The flame not only advances into and transforms the explosive mixture but simultaneously it is carried bodily outward by the expansion of the gases within it. Stevens (7) showed that the transformation velocity  $S_t$  may be computed from the speed in space and expansion ratio through the relation

$$S_t = \frac{S_s}{E} \quad (3)$$

Values of  $E$  may also be used to calculate the temperature of the hot gases at the instant the flame has completed its travel, if sufficient equilibrium data are available from the other sources (2).

It was known, prior to the application of the bubble method, that water vapor had a large effect upon the speed of flame in space in mixtures of carbon monoxide and oxygen. For this reason it was necessary to control the quantity of water vapor in the explosive mixtures during the formation and life of the bubbles. It was found by Fiock and Roeder that the transfer of water vapor to or from the atmosphere surrounding the bubble was quite rapid, and that the partial pressure of water vapor had to be made identical in the mixture, the soap solution, and the surrounding air. This was accomplished by blowing the bubbles at the center of a large chamber at a controlled temperature and humidity corresponding to the vapor pressure of the soap solution.

#### *Effect of fuel-oxygen ratio*

Since the experiments of Stevens were made without adequate control of the moisture content of the air in which the bubbles were blown, some of his measurements were repeated with more accurate control of conditions. Figure 4 shows the effect of mixture ratio upon flame speeds and expansion ratio for various mixtures of carbon monoxide and oxygen, each initially at 25°C. and containing 2.69 per cent of water vapor by volume. The plotted values of  $E$  and  $S_s$  were calculated directly from measurements on the photographic records. Values of  $S_t$  were obtained from the smooth curves for  $S_s$  and  $E$ .

As a result of a large number of experiments on the system carbon monoxide-oxygen it has been concluded that both  $S_s$  and  $S_t$  have maximum values slightly on the rich (in carbon monoxide) side of chemical equiva-



lence. Values of  $E$ , however, change so little on either side of equivalence that it is impossible to locate the maximum from the data available.

All experience indicates that the mechanics of the explosion in a soap film and the method of analyzing the results were correctly postulated by Stevens. However, he concluded that the speed of flame relative to the unburned gas was directly proportional to the mass action product of the concentrations of the active constituents in the original mixture. Applied specifically to the explosive oxidation of carbon monoxide, this statement

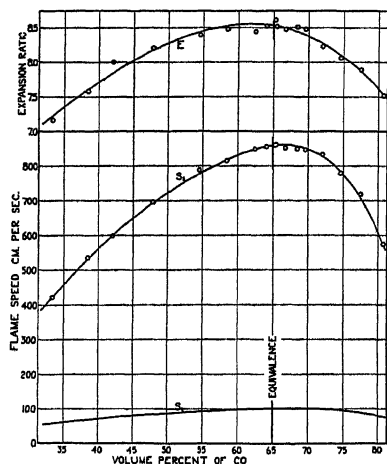


FIG. 4

FIG. 4. Effect of fuel-oxygen ratio on combustion characteristics of mixtures of carbon monoxide and oxygen. ( $H_2O = 2.69$  per cent.)

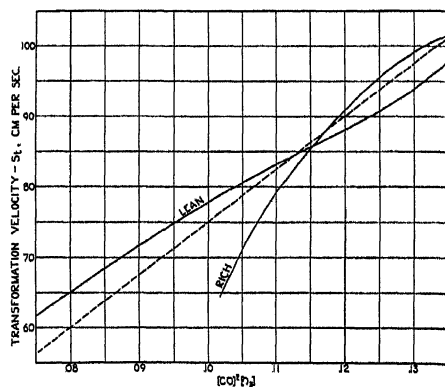


FIG. 5

FIG. 5. Relation between transformation velocity ( $S_t$ ) and the mass action product for mixtures of carbon monoxide and oxygen. ( $H_2O = 2.69$  per cent.)

means that the relation between  $S_t$  and the initial concentrations of carbon monoxide and oxygen is expressed by the equation,

$$S_t = k[CO]^2[O_2] \quad (4)$$

in which  $k$  is a constant for each value of water vapor content and the bracketed symbols indicate concentrations of the reactants. The more precise data fail to confirm this relation. Instead of being directly proportional to the mass action product, the transformation velocity varies with it in the complex manner shown in figure 5. The equation, regardless of the value of  $k$ , gives a maximum value of  $S_t$  at exact equivalence, while the observed maximum values of both  $S_s$  and  $S_t$  are definitely on the rich side of equivalence. It therefore seems necessary to abandon Stevens' concept

of the proportionality of  $S_i$  to the initial composition and to resume the search for a relation which is in better accord with the observed facts.

Mixture ratio affects not only flame speed but also the intensity of the light emitted by the explosion. The density of the photographic records decreases on either side of equivalence, as shown in figure 6. On the lean

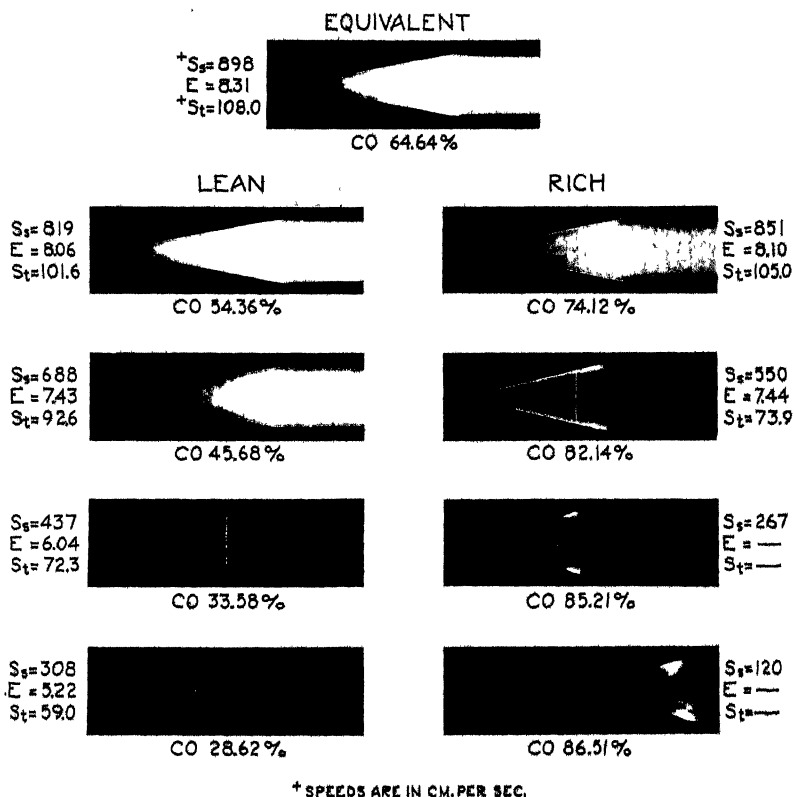


FIG. 6. Photographic records of explosions in bubbles for various mixtures of carbon monoxide and oxygen. ( $H_2O = 3.31$  per cent.)

side, in the range near equivalence, the afterglow seems to emit more actinic light than the flame front. On the rich side the afterglow soon becomes very faint, then disappears entirely. At both extremes the flame front appears on the records as a line of much greater density than the image of the hot gases which are surrounded by the reaction zone. For very rich mixtures a somewhat irregular flame appears after the excess of

fuel has mixed with the oxygen of the surrounding air. In such cases the measurement of final volume (and hence also of  $E$  and  $S_t$ ) is impossible.

### *Effect of inert gases*

Figure 7 shows the effect on flame speed and expansion ratio of replacing various portions of the active gases carbon monoxide and oxygen with helium or argon. The ratio of carbon monoxide to oxygen had the constant value of 1.811 and the water vapor content was 2.69 per cent throughout. Since it is necessary in the bubble method to hold the moisture content of the mixture constant, the ratio of water vapor to active gas

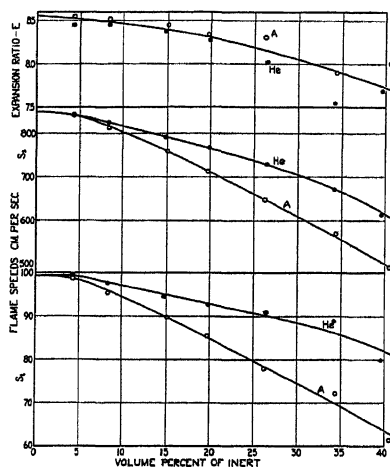


FIG. 7

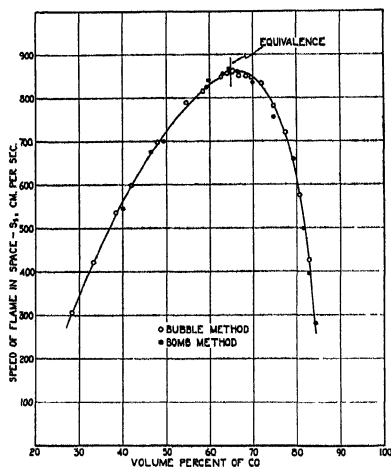


FIG. 8

FIG. 7. Effects of argon and helium on combustion characteristics of mixtures of carbon monoxide and oxygen. ( $\text{CO}/\text{O}_2 = 1.811$ ;  $\text{H}_2\text{O} = 2.69$  per cent.)

FIG. 8. Speed of flame in space for various mixtures of carbon monoxide and oxygen as determined by the bomb and bubble methods. ( $\text{H}_2\text{O} = 2.69$  per cent.)

increased as more inert gas was added. From other experiments it is known that such an increase in the proportion of water vapor causes a decrease in  $E$  and an increase in  $S_s$  and  $S_t$ . Thus the decrease in  $E$  would have been less and the decrease in  $S_s$  and  $S_t$  would have been more than that shown by the curves if the ratio of the concentration of carbon monoxide and water vapor could have been kept constant. Similar results have been obtained at various other ratios of carbon monoxide to oxygen (3).

The decrease in  $E$  with increasing concentration of inert gas is due to the fact that less active mixture and therefore less heat is available to raise

the temperature of the same volume of gas. However, the specific heats of both argon and helium are much lower than that of the carbon dioxide which they replace in the final combustion products. Also the lower final temperature permits a greater conversion of carbon monoxide and oxygen to carbon dioxide and reduces the heat lost by radiation. Because of these effects  $E$  decreases more slowly than does the concentration of the active mixture. Interpreted in terms of engine performance, the addition of inert gas would tend to decrease the maximum power available but should increase the efficiency of fuel utilization.

Regardless of the mechanism by which flame propagates, the replacement of active mixture by inert gas may be thought of as the introduction of a resistance, in the form of intermediate collisions, to the transfer of energy in some form from the flame to the unburned gas. The magnitude of the resistance depends upon characteristics of the inert gas which have not yet been definitely identified. Such a resistance is doubtless responsible for the observed decrease in transformation velocity with increasing concentration of inert gas.

Direct comparisons of the effects of like volumes of argon and helium are possible from data at hand. These data show that both argon and helium have practically the same effect upon expansion ratio, but very different effects upon flame speed. For all values of the ratio  $\text{CO}/\text{O}_2$  from 0.5 to 3.8, a given volume of helium produces a smaller decrease in flame speed than a like volume of argon. The differences in both  $S_u$  and  $S_b$  produced by like volumes of argon and helium are independent of the fuel-oxygen ratio and approximately proportional to the concentration of inert gas.

#### CONSTANT-VOLUME EXPLOSIONS

##### *Measurements of the speed of flame in space*

When an explosion in a closed bomb with transparent walls is photographed, the initial portion of the flame record is identical with that obtained by the bubble method, although the movement of the flame is subsequently modified by the restraining effect of the bomb walls. Figure 8 compares flame speeds in space as determined by the bubble method with corresponding speeds for the same mixtures fired in a bomb made from a glass cylinder 6 in. in diameter and 6 in. long, with metal disks and rubber gaskets sealing the ends. The two sets of data agree within the experimental error.

Substitution of a constant-volume bomb for the soap film makes it possible to vary the water vapor content and the pressure of the mixture independently. Figure 9 shows the effect upon  $S_u$  of changing the moisture content in equivalent mixtures of carbon monoxide and oxygen at a number

of initial pressures. The explosions at atmospheric pressure were made in the cylindrical bomb just mentioned. The data at lower pressures were obtained in a 5-liter spherical glass flask. Both bombs were provided with central ignition.

From mixtures too dry to ignite or photograph properly to those which were saturated with water vapor at room temperature and the pressure of the experiment, an increase in moisture content always produced an increase in flame speed. Successive equal increments of moisture have diminishing effects upon flame speed, and there is doubtless some concentration beyond which further addition of water vapor will produce a decrease in flame speed. If it had been practicable to maintain the explo-

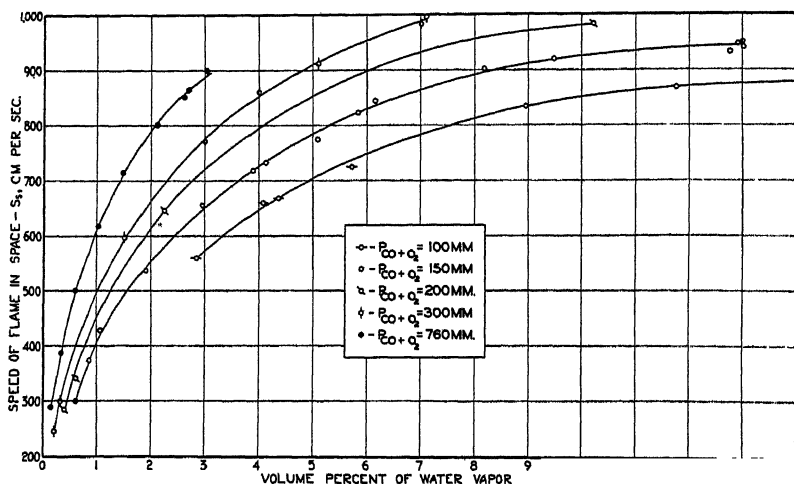


Fig. 9. Effects of water-vapor content and initial pressure on speeds of flame in space for equivalent mixtures of carbon monoxide and oxygen.

sion vessel at an elevated temperature, it is believed that this concentration might have been reached at each of the dry-gas pressures studied. Figure 9 shows also that equal increments of moisture cause more increase in flame speed at the higher pressures. It is quite evident that water-vapor content must be carefully controlled and specified if determinations of flame speed in mixtures of carbon monoxide and oxygen are to be significant.

In normal photographic records of comparatively fast-burning mixtures of carbon monoxide and oxygen, fired in either a soap bubble or bomb, the flame appears to attain its maximum velocity in space at the instant of the spark. If, however, the film is moved at an abnormally high speed, the records show that there is a very short interval, just after ignition, in

which the flame has a positive acceleration, as evidenced by the curvature of the traces. The diagram on the right in figure 10 shows this early period of flame travel on a magnified scale.

The straight portion of the flame trace  $SF$  may be extended until it intersects at point  $A$  the axis  $SD$ , drawn through the spark  $S$ . The time interval  $SA$  is the increase in the duration of the explosion caused by the initial slow movement of the flame and will be termed briefly the "delay."

The curve of figure 10 shows that the delay increases greatly as the concentration of water vapor is reduced in equivalent mixtures of carbon

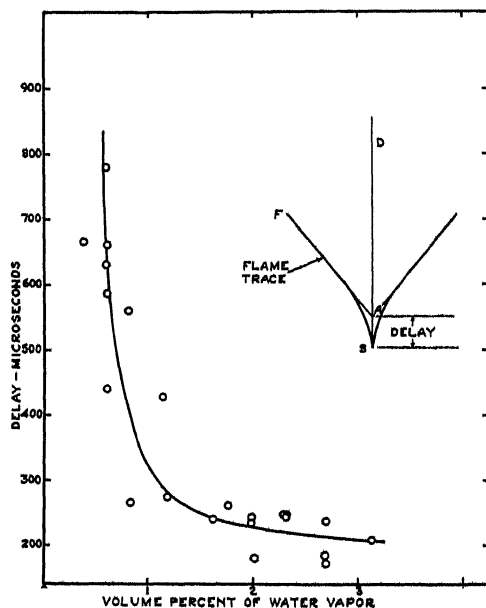


FIG. 10. Effect of moisture content on the delay period for equivalent mixtures of carbon monoxide and oxygen at atmospheric pressure.

monoxide and oxygen, initially at atmospheric pressure. Reducing the pressure at constant water-vapor concentration also increases the delay markedly, but quantitative measurements are difficult because of the decrease in the actinic light emitted by the explosions.

The real significance of the delay period is not known. It is possible that the low initial speeds of flame in space result chiefly from subnormal values of  $E$ , which in turn may be associated with the establishment of an equilibrium depth and structure of the reaction zone. If the normal reaction zone has a considerable depth, the flame front must travel at least this same distance from the point of ignition before the equilibrium

structure is established. Previous to the attainment of such an equilibrium state, both  $S_t$  and  $E$  may be abnormally low and increasing toward their normal values.

*Proposed experimental method*

While flame records obtained in constant-volume bombs yield, directly, values of the speed of flame in space, means for measuring the rise in pressure must be provided if values of transformation velocity are to be obtained. Lewis and von Elbe (4) have derived values of this property for

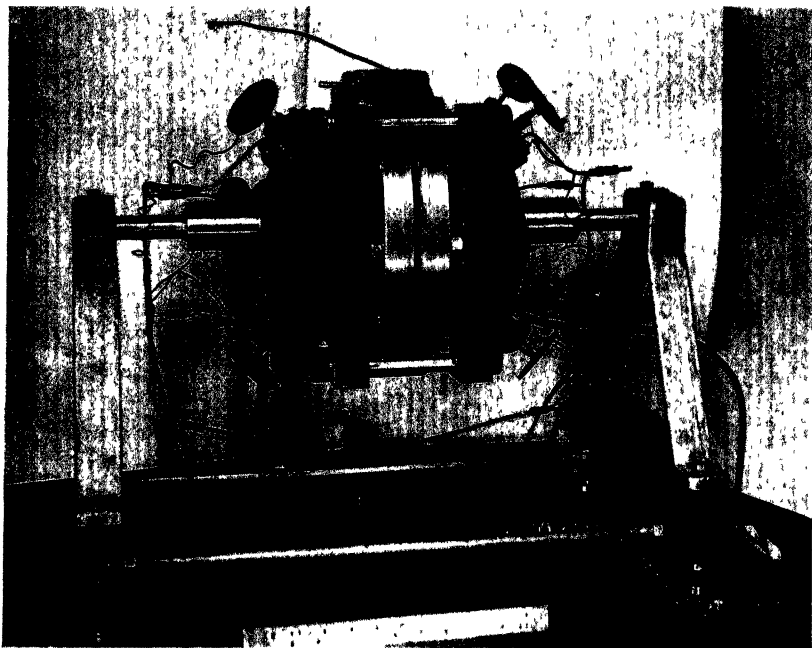


Fig. 11. Spherical steel bomb equipped to yield simultaneous records of flame travel and pressure development.

ozone explosions from time-pressure records alone. However, if experimental records of both flame travel and pressure development are obtained, the observed quantities can be reduced to the desired properties in a simpler and more positive manner. A spherical bomb and auxiliary equipment designed to yield these two records simultaneously have been constructed at the National Bureau of Standards.

This bomb, shown in figure 11, is composed of two flanged hemispheres of stainless steel, clamped together upon a short cylindrical ring of glass. It is mounted with a narrow window in the vertical position so that the

presence or absence of convective rise during burning may be detected. The spread of flame from the central point of ignition is photographed on a rotating film as in the bubble experiments. Six diaphragm indicators are provided to measure the rise in pressure which is recorded on the film with the flame trace.

Figure 12 is a diagrammatic representation of the spherical bomb with its window, and includes a comparison of typical flame traces for bomb and soap bubble.

When a spark occurs at the center of the bomb, a sphere of flame starts to spread exactly as in the constant-pressure explosion. However, the walls of the bomb soon resist the outward flow of gas set up by the expansion, and the unburned charge is compressed instead of merely being moved away by the advancing flame front. Thus the expanding gases cannot

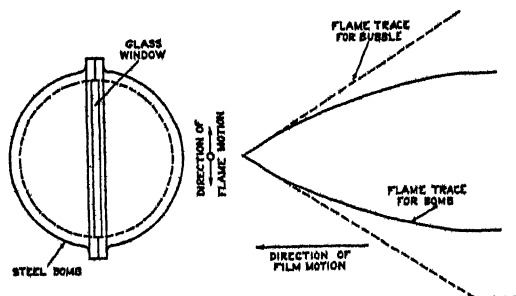


FIG. 12

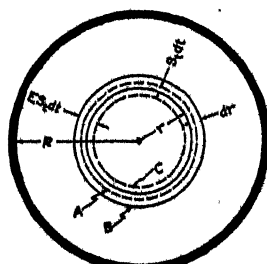


FIG. 13

FIG. 12. Comparison of flame records obtained in the bomb and bubble methods  
FIG. 13. Diagrammatic section indicating the significance of mathematical terms

push the flame front outward as fast or as far as in the bubble explosion. As a result of the steadily decreasing outward gas velocity, the flame front travels more slowly as it approaches the walls, even though it may be propagating into the compressed and heated unburned charge at an ever-increasing speed.

The slopes of the flame traces shown in figure 12 constitute a direct measure of the speeds of flame in space. The slope of the trace of the flame in the bomb gradually decreases from the constant value of that in the bubble until it reaches a value at the wall which is a measure of the transformation velocity of the last portion of the charge to burn. This condition must always prevail since the last of the gas to burn cannot move beyond the walls, and is, therefore, essentially at rest when traversed by the flame.

Consider, as illustrated in figure 13, that the flame front, in a spherical



bomb of radius  $R$ , has a radius  $r$  at time  $t$  after ignition. In the next increment of time  $dt$ , the reaction zone will transform a shell of gas of thickness  $S_t dt$ , which, upon expansion, will advance the flame front a total distance  $dr = S_t dt$ . Thus the remaining unburned gas is compressed from an inner boundary represented by the dotted line  $A$  to one represented by the solid line  $B$ , with an accompanying rise  $dp$  in pressure.

Applying the adiabatic law in differential form to this compression of the unburned charge gives

$$\frac{dp}{p} = \frac{-k_u dV_u}{V_u} = \frac{-3k_u r^2 (S_t dt - dr)}{R^3 - r^3} \quad (5)$$

in which  $k$  is the adiabatic exponent,  $V$  is total volume, and the subscript  $u$  refers to the unburned gas.

Equation 5 reduces to the form

$$S_t = S_s - \frac{(R^3 - r^3)}{3pk_u r^2} \frac{dp}{dt} \quad (6)$$

If  $E$  is the expansion ratio at time  $t$  and pressure  $p$ , the shell of unburned gas of thickness  $S_t dt$  will expand, upon burning, to a volume of  $4\pi r^2 E S_t dt$ , compressing the previously burned gas to an outer boundary represented by dotted line  $C$  in figure 13. The observed increase in total volume of the burned gas is only  $4\pi r^2 dr$ , and the actual change in volume of the previously burned gas is therefore the difference  $4\pi r^2 (dr - E S_t dt)$ .

Applying the adiabatic law now to the compression of the previously burned gas, using the subscript  $b$  to designate properties of gas in this state,

$$\frac{dp}{p} = \frac{-k_b dV_b}{V_b} = \frac{3k_b (E S_t dt - dr)}{r} \quad (7)$$

which reduces to

$$E = \frac{1}{S_t} \left[ \frac{r}{3pk_b} \frac{dp}{dt} + S_s \right] \quad (8)$$

The recompression of the burned gas by the subsequent expansion of surrounding layers is complicated by the shifts in equilibrium that accompany the compression and by the existence of both temperature and concentration gradients. When the burning has progressed to the stage where these effects are no longer negligible, it is difficult, if not impossible, to fix upon a value of  $k_b$  which will accurately represent the compression of the burned gases. However, the value of  $k_b$  has only a small effect upon the calculated value of  $E$  for the early stages of the explosion. Thus reliable values of  $E$  at the initial condition may be had, even though the selected value of  $k_b$  is somewhat uncertain. When the dissociation is

negligible or calculable, the temperature, density, and concentration gradients which exist in the burned gas may be evaluated by a method such as that developed by Mache (5) and applied by Lewis and von Elbe (4) in obtaining numerical results for ozone-oxygen explosions.

The quantity  $\frac{dp}{dt}$  may be eliminated from equations 6 and 8, yielding the equation

$$ES_i = S_s + \frac{k_u r^3}{k_b} \frac{(S_i - S_s)}{(R^3 - r^3)} \quad (9)$$

If the explosion takes place at constant pressure,  $R$  is infinite and equation 9 reduces to  $ES_i = S_s$ , which is the relation (equation 3) used in calculating  $S_i$  from the bubble experiments.

The conditions existing in the unburned gas at any instant may be calculated from the observed value of pressure, through the adiabatic law. From the experimentally determined variations of pressure and flame radius with time, values of the slopes  $\frac{dr}{dt} = S_s$  and  $\frac{dp}{dt}$  may be found for any value of  $p$ ,  $r$ , or  $t$  during an explosion at constant volume. Accurate values of  $k_u$  are available in the literature.

During an explosion at constant volume there will be a loss of heat from the layer of unburned gas nearest the walls of the bomb, tending to cause an ever-increasing departure from adiabatic compression as the temperature, density, and fraction of the remaining unburned gas in contact with the walls increase. On the other hand, the unburned gas may absorb some of the radiant energy from the flame, either directly or after it is reflected from the polished walls of the bomb. In the final stages of the explosion, preflame reactions may supply heat to the unburned charge. Since the total time of burning is very short, these effects are probably very small individually, and since they are not all in the same direction, their net effect will also be small. Certainly they may be ignored during the earlier stages of the explosion when temperature rises very little.

It is only during the very late stages of the burning that the temperature and pressure of the unburned gas change greatly. Here the departures from true adiabatic compression undoubtedly become appreciable, and the temperature of the unburned gas, as calculated from the observed pressure, is far less certain. Despite this fact, it is evident from equation 6 that the calculated values of  $S_i$  do not decrease in accuracy, because the term

$$\frac{(R^3 - r^3)}{3pk_u r^2} \frac{dp}{dt}$$

assumes a rapidly diminishing importance as  $r$  approaches  $R$ .

Some very short but finite time will elapse before the rise in pressure, that starts at ignition, reaches pressure indicators at the walls of the bomb. During this brief interval there will be no recorded rise in pressure, the experimental values of  $\frac{dp}{dt}$  will be zero, and the value of  $S_t$  calculated by equation 6 will be identical with  $S_u$ , which is, of course, absurd. However, when the flame speed is well below the velocity of sound, the pressure gradients in the bomb are extremely small and soon become a negligible portion of the pressure rise, whereupon equation 6 becomes valid. Since it appears probable that errors due to non-uniformity of pressure will become negligible before the rise in pressure and temperature of the unburned charge is sufficient to cause significant change in  $S_t$  and  $E$ , there

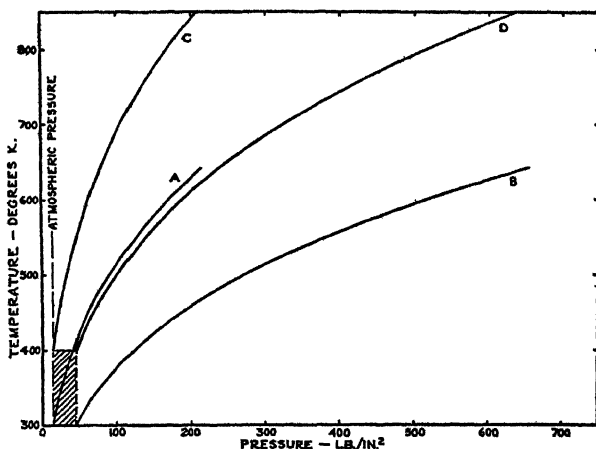


FIG. 14. Simultaneous rise in temperature and pressure resulting from the adiabatic compression of an equivalent mixture of carbon monoxide and oxygen from various initial states.

should be no necessity for attempting to evaluate the very early portion of the pressure curve.

Although the separate effects of charge temperature and pressure cannot be isolated from data on a single explosion, this may be done over a comparatively wide range by varying the initial conditions over a much smaller range.

Curve A of figure 14 shows the simultaneous rise in temperature and pressure of the unburned gas due to compression by the flame of an equivalent mixture of carbon monoxide and oxygen, originally at 300°K. and 1 atm. If the initial temperature is maintained at 300°K. and the pressure is varied between 1 and 3 atm., the range between curves A and B can be studied without special temperature control. If the initial temperature

is  $400^{\circ}\text{K.}$ , a pressure variation of from 1 to 3 atm. permits study of the range between curves C and D. Thus by varying the initial temperature and pressure in the comparatively small range indicated by the shaded rectangle, the entire region between B and C may be investigated. Since most points in this region may be reached from two or more different initial states, opportunity for correlating results at different stages of the explosion is provided.

### *Pressure measurement*

The utility of time-pressure records of explosions at constant volume has already been cited. Since the accuracy of the derived values of trans-

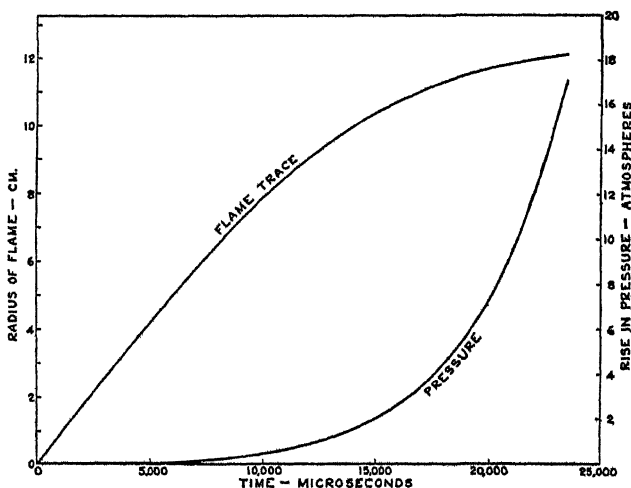


FIG. 15. Calculated time-displacement and time-pressure curves for the explosion of an equivalent mixture of carbon monoxide and oxygen in a spherical bomb of radius 12.2 cm. ( $\text{H}_2\text{O} = 2.69$  per cent.)

formation velocity depends, among other things, upon that of the pressure measurements, these will be discussed briefly by referring to the method which is being used at the National Bureau of Standards.

Figure 15 shows calculated time-displacement and time-pressure records for an explosion in a spherical bomb of an equivalent mixture of carbon monoxide and oxygen, initially at  $300^{\circ}\text{K.}$  and 1 atm. It will be noted that the pressure rises only about 0.2 atm. while the flame traverses half the distance to the wall, and that it rises by about 14 atm. during the last tenth of the travel. To obtain accurate results for the entire explosion it is necessary to measure accurately both the very small rise in pressure during the early stages and the high and rapidly rising pressure near the end.

The diaphragm type of pressure indicator was selected for its inherent simplicity, adaptability, and high precision. Preliminary experiments indicated that any sort of passage between the explosion chamber and the diaphragm of the indicator, even a well-perforated backing plate, is undesirable where high precision is required and fast-burning mixtures of high energy content are used.

The indicator, as shown in figure 16, is therefore constructed so that the diaphragm forms part of the combustion chamber wall. An insulated electrode can be adjusted to make contact with the diaphragm when the pressure in the bomb has reached any desired value. When contact is

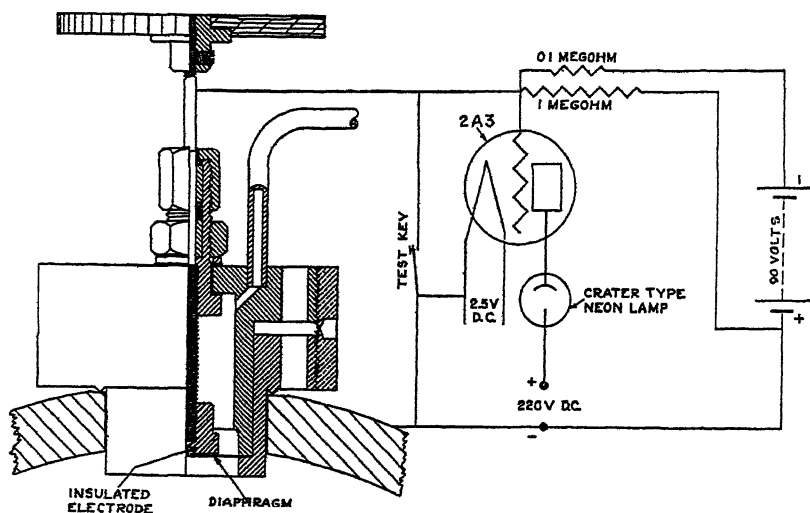


FIG. 16. Diaphragm pressure indicator, with recording circuit and lamp, designed for use with spherical bomb.

made, the negative bias on a vacuum tube (2A3) acting as a relay is reduced, permitting a larger current to flow through the plate circuit of the tube and a crater-type neon lamp. The lamp has a negligible time lag and may be readily photographed on the same film with the flame trace. A record is thus obtained of the instant that the predetermined pressure is attained in the bomb. Six similar indicators provide for recording six points on the time-pressure curve for each explosion, and several explosions from identical initial conditions will be required to establish the entire pressure curve.

In an indicator of the type shown in figure 16, the diaphragm need be

only strong enough to withstand the pressure to be measured, for it is supported by the electrode after contact is made. The space behind the diaphragm is normally open to the atmosphere, and the diaphragm makes contact after being deflected elastically by the pressure in the bomb. However, the space behind the diaphragm may be sealed if desired and a backing pressure applied to give the diaphragm an initial deflection into the bomb. If the electrode has been previously set to make contact when the diaphragm returns to its neutral position, the indicator will record the instant at which the pressure in the bomb is equal to the known constant backing pressure. In either case, the indicator may be calibrated in place, just before use, by setting the electrode, slowly increasing the pressure in the bomb until contact occurs, and measuring the pressure.

The only sources of significant error in an indicator of this type are variations in the static pressure required to cause contact on repeated trials and excessive inertia of the diaphragm, which would cause it to assume different positions under static and dynamic conditions. Preliminary tests with the six indicators mounted in the spherical bomb are being conducted to determine the diaphragm dimensions required for adequate strength and a satisfactory compromise between high reproducibility and low inertia error in different portions of the pressure range.

#### CONCLUSIONS

To be of greatest usefulness, a method for measuring flame speed must yield values of transformation velocity, which is the speed of flame in a direction normal to its surface and relative to the unburned charge. Of the various methods which have been used, those employing spherical flames are probably susceptible of the most rigorous analysis. Transformation velocities may be determined for explosions producing spherical flames either at constant pressure or at constant volume.

In both methods adequate control of the composition of the mixtures must be provided and all components must be gases or vapors. The light emitted by the explosions must be sufficiently actinic for photographic purposes. Flame speeds must not be so high that excessive pressure gradients are developed ahead of the flame front, or so low that convective rise is apparent during the explosion. Each method has, in addition, its individual advantages and limitations.

The constant-pressure or bubble method for measuring flame speeds has the great advantage that it requires the measurement neither of rapidly changing pressure nor of gas flow. All results are derived from a simple photographic record of flame spread which is rapidly obtained and easily analyzed. The value of the speed of flame in space as obtained by this method is a characteristic property of the explosive mixture dependent

only upon its transformation velocity and expansion ratio. Under favorable conditions all three of these properties can be evaluated by the bubble method, with a precision which is probably equal or superior to that attainable by any other method.

The principal disadvantage of the bubble method is that the partial pressure of water vapor in the explosive mixture is fixed by the temperature and composition of the soap film. It is therefore not practicable to maintain the temperature constant while the effect of variation in water vapor content is studied, or to maintain a constant ratio of moisture to active charge while temperature, pressure, and extent of dilution by inert gases are varied independently. This limitation is especially serious when the water is involved in the combustion reactions, as in mixtures of carbon monoxide and oxygen.

Materials of the soap film must not react with or dissolve any constituent of the explosive mixture and thus cause significant changes in its composition. In very rich mixtures the excess fuel burns in the surrounding atmosphere after the flame front has completely traversed the original mixture. In such cases values of transformation velocity and expansion ratio cannot be determined.

The spherical bomb of constant volume is adapted to the measurement of flame speeds over much wider ranges of charge composition, pressure, and temperature than is feasible with the bubble method. Charge composition may be varied at will, so long as all constituents are gases or vapors. The independent effects of pressure and temperature upon flame speeds may be isolated over a considerable range by making relatively small changes in initial pressure only, and the range may be greatly extended if provision is made for moderate variation of initial temperature. Conditions in the spherical bomb may thus be made to approach those prevailing in an engine, but greater opportunity exists for independent variation and control of conditions.

The gross mechanism of an explosion at constant volume is much more complex than for one at constant pressure, a more complicated apparatus and procedure are required for the determination of transformation velocity, and there is greater opportunity for error in the results. Perhaps the greatest single difficulty is in the accurate measurement of pressure. Indicators should be capable of recording faithfully both the very small initial rise in pressure during the early stages of the explosion and the high and rapidly rising pressures near the end. The necessity for evaluating slopes of the flame-travel and pressure-development curves involves errors which vary in magnitude with the position of the flame front. Greatest error in the results would be expected in the very early and very late stages.

It is hoped that future measurements of flame speed, through further development and use of both methods, will provide basic information which will clarify the mechanism of flame propagation and suggest practical means for further control of gaseous explosions. It is believed that such studies will yield results of many types, any or all of which may contribute to our knowledge of the combustion process and aid in its further improvement as a source of power in engines.

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# PROBLEMS OF STATIONARY FLAMES<sup>1</sup>

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## I. INTRODUCTION

It is the purpose of this paper to present, semiquantitatively, a number of the problems involved in the measurement of flame speeds by burner methods, and some fundamental problems connected with the utilization of stationary flames by means of burners of several kinds. Since the burner is the control device by means of which the flame is made to function, the problems and uses of stationary flames are bound up inextricably with it. Of the various factors to be considered in the manipulation of stationary flames, it is becoming increasingly apparent that flame speed plays the dominant rôle and that it usually appears as the determining factor in the behavior of the flame.

It is unfortunate that burner methods of measuring flame speeds appear to be reliable within only a limited range of operating conditions. The methods are relatively simple, and within their limitations the results apply directly to a multitude of problems involving flames and burners. Some of these problems are presented very briefly, merely for illustration and without any attempt at exhaustive treatment.

## II. FLAME SPEEDS BY BURNER METHODS

### *A. Brief review of methods of measurement and computation*

When measurements of flame speed were first undertaken by burner methods, Bunsen (3) assumed that the downward velocity of the flame front just exceeded the upward velocity of the gas mixture at the moment when the flame flashed back down the burner tube. Obviously this could be true only if the velocity were uniform across the stream of gas mixture.

Gouy (7) at first considered the flame speed to be equal to the product of the velocity of the gas mixture and the sine of the angle which the side of the flame cone made with its axis. Then, finding that the surface formed by the flame front did not approximate sufficiently to a true cone

<sup>1</sup> Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce.

(see figure 1) and that the result obtained depended upon what part of the flame front he used when he measured the angle, he eliminated the angle from consideration by setting the velocity of the flame equal to the volumetric rate of flow of the mixture divided by the area of the flame surface. This involves the concept of flame speed as simply the rate of transformation of the mixture, without the necessity of considering the velocity of the gas mixture and its direction of flow. The two concepts would yield identical results if the flame surface were a geometrical cone with the burner port for a base.

Gouy determined the area of the flame surface from measurements of the image of the flame projected on a screen. Considering the figure as a surface of revolution, he obtained the area by integration.

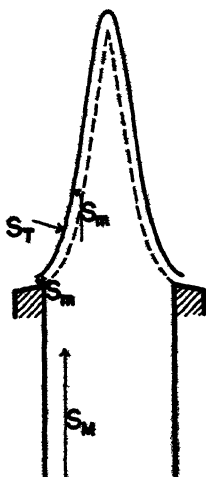


FIG. 1. Shape of typical flame surface

Michelson (8) also measured the volumetric rate of flow of the mixture and determined the actual area of the "cone" by treating measurements of enlarged photographs in the same way that Gouy had done.

Ubbelohde and Koelliker (15) concluded that the rounded tip and the curved base of the flame surface represented deviations from what they termed the "normal" flame velocity, so they measured the angle made by the "straight" portion of the flame surface with its axis, and computed the result as Gouy had done originally.

Stevens (13) was unable to obtain results with the burner which were in satisfactory agreement with the results he obtained with the "bubble" when he determined the area of a flame surface as Gouy, Michelson, or Ubbelohde had done. He recognized, as did Ubbelohde, that the approxi-

mately conical flame surface was the resultant of several components, one of which was a mixture velocity which varied from practically zero at the walls of the burner tube to a maximum at the center. Stevens, therefore, made use of only that part of the flame surface which resulted from the portion of gas mixture whose actual linear velocity was equal to the mean velocity over the cross section of the stream. He constructed on the photograph of a flame a triangle having as its base the diameter of the burner port and its sides parallel to the tangents to the flame surface at the part where the velocity of the mixture equaled the mean velocity. Considering this triangle as a section through the axis of a cone, the area of the cone was easily calculated without integration from the measured altitude and base, and values obtained from it for the velocity of the

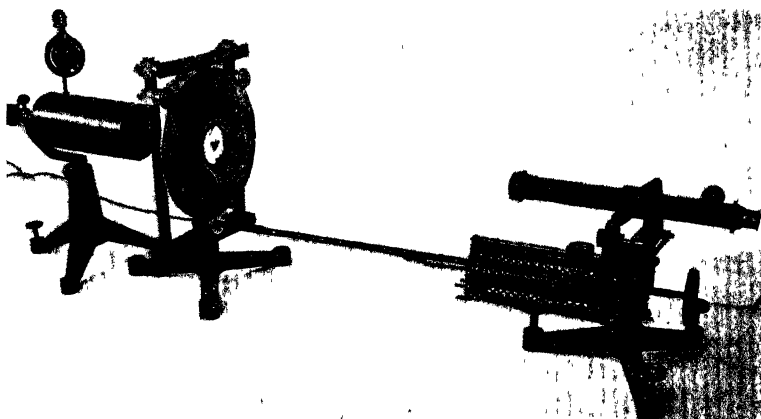


FIG. 2. Goniometer and reading telescope for measuring the angle between the two sides of the flame surface

flame front relative to mixtures of carbon monoxide and oxygen agreed with those obtained with the bubble so closely that the two methods, for many purposes, could be used interchangeably.

A number of other workers have adhered to Gouy's assumption, expressing flame speed in terms of volume of combustible mixture per second divided by the area of the flame surface. Of these, some use the actual integrated area of the flame surface and others use the area of a geometrical cone having the burner port as a base. The area of this geometrical cone has been arrived at in various ways, which have no bearing on what follows and will not be discussed here.

Since the area of the burner port divided by the lateral area of a geometrical cone of which the burner port forms the base is equal to  $\sin \alpha$  (where  $\alpha$  is the angle between the side and the axis of the cone), the cone may also

be defined by the area of the burner port and the angle  $\alpha$ . All of these expressions would lead to the same numerical result were the flame surface a geometrical cone.

Instead of measuring and computing the area of the cone as Stevens had done, Smith and Pickering (12) chose to measure directly the angle  $\alpha$  between the tangents and the axis, which, together with the burner port, is sufficient to define the cone. Instead of dividing the volumetric rate of flow of the combustible mixture by the area of the cone to obtain the flame speed, the rate was divided by the area of the burner port, thus obtaining the average linear velocity of flow of the mixture. The angle was measured, with the instrument shown in figure 2, at that part of the flame surface where the local velocity of flow of the mixture was equal to the average velocity, i.e., at a point  $0.7r$  from the axis. The sine of the angle  $\alpha$ , multiplied by the average velocity of the mixture ( $S_M$ ), then gave the same numerical value for the flame speed ( $S_T$ ) as did Stevens' method. The velocity of propagation of the flame front, in a direction normal to its surface and relative to the combustible mixture in which it moves, was then given by the equation  $S_T = S_M \sin \alpha$ .

*B. The influence of several experimental factors on the numerical result for the flame speed*

In any combustible mixture of gases of given composition, temperature, and pressure, there is a definite fixed value for the flame speed relative to the gas mixture. Consequently, if different values are obtained by different means, it must be concluded either that one of the supposedly fixed experimental conditions was not what it was supposed to be, or that the differences in the numerical result have been imposed by differences in the methods of measurement and computation, or by the apparatus.

On this basis the degree to which the numerical result is found to be independent of the method or apparatus for obtaining it may be used as a criterion of the extent to which that result approaches the supposedly correct definite fixed value assumed above to exist.

1. The numerical result is independent of the velocity of flow of the mixture, so long as the flow is laminar

With a given combustible mixture, a high velocity of flow from the port results in a long narrow flame and *vice versa*. The results presented in table 1 show that, all other conditions remaining substantially constant, the flame speed,  $S_T$ , is unaffected by changes in the mixture velocity which range from incipient flashing back to incipient blowing off of the flame.

Ubbelohde and Koelliker (15) studied the effect with mixtures of hydrogen and air. The maximum-speed mixtures showed the same flame speed

until the mixture velocity reached 1300 cm. per second, which corresponds to a Reynolds number,<sup>2</sup>  $R$ , of over 2400. Since at the critical velocity  $R = 2300$ , the flow was probably no longer laminar but turbulent. This undoubtedly accounts for the increased value of the flame speed which they found at higher velocities.

2. The result depends upon the size of the port, especially if the area of the flame is used in obtaining the result

Several workers, including Ubbelohde and Koelliker (15), have concluded that burners of different sizes yield different results. Ubbelohde and

TABLE 1  
*Effect on  $S_T$  of changing the velocity of the same mixture*

GAS IN MIXTURE	VELOCITY OF MIXTURE $S_M$	FLAME SPEED $S_T = S_M \sin \alpha$
(A) 9.60-mm. burner. Propane-air		
<i>per cent</i>	<i>cm. per second</i>	<i>cm. per second</i>
4.76	64.4	33.9
4.69	87.2	34.5
4.59	111.7	33.9
4.54	131.2	33.5
4.41	155.9	34.3
4.38	178.4	32.7
(B) 2.75-mm. burner. City gas-air		
17.55	221.7	46.3
17.56	209.4	47.2
17.48	193.3	47.2
17.47	171.3	46.0
17.57	150.4	46.6
17.53	128.8	47.9

Hofsäss (14) state that the error is larger with small burners and both agree that it tends to disappear as the composition of the mixture approaches that for maximum flame speed. Corsiglia (4), however, states that different sizes of burners yield the same result within the limit of experimental error. Smith and Pickering (12), for comparison, computed the flame speed from measurements of twelve flames by the method of Corsiglia as well as by their own.

$$R = DVd$$

where  $D$  = diameter of burner tube expressed in centimeters,  $V$  = velocity of fluid in centimeters per second,  $d$  = density of fluid in grams per cubic centimeter, and  $\mu$  = viscosity of fluid in c.g.s. units.

Figure 3 shows curves representing the flame speed in each of three mixtures. Set A contained 62 per cent of the air required for complete combustion of the gas, set B 90 per cent (maximum  $S_T$ ), and set C 103 per cent. Each mixture was used with four burners having internal diameters of 2.75, 4.45, 6.50, and 9.60 mm., respectively. Within each set the value

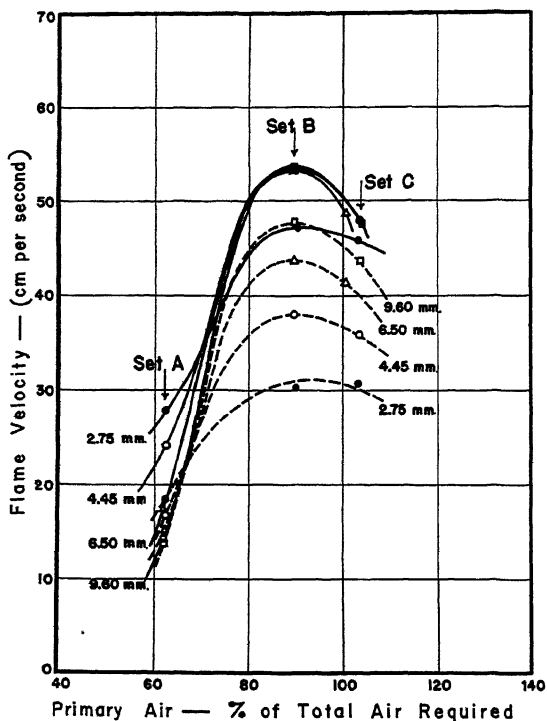


FIG. 3. Flame-speed curves. Composition, temperature, pressure, and  $S_M$  constant within each set. The solid curves result from measurements of the angle. The dotted curves result from measurements of the area of the flame surface by the method of Corsiglia.

of  $S_M$ , as well as the temperature and composition of the mixture, was kept constant as the size of the port was changed.

The solid curves result from measurements of the angle by the method of Smith and Pickering (12). With the maximum-speed mixture, the same result is obtained on the three larger burners, within the limit of experimental error. The 2.75-mm. burner is about 11 per cent lower. In the other mixtures, especially in set A with the low primary air, the results with the different burners are widely divergent. The broken

curves result from measurements of the area of the flame surface, on the same photographs, by the method of Corsiglia (4). The results from the different burners are widely divergent in the maximum-speed mixture, but agree very well at about 67 per cent of the total air required. The reasons for such divergent results will be apparent from the next two figures.

Figure 4 shows the four flames of each set and the relative sizes and shapes which result when  $S_M$  and composition are kept constant within each set.

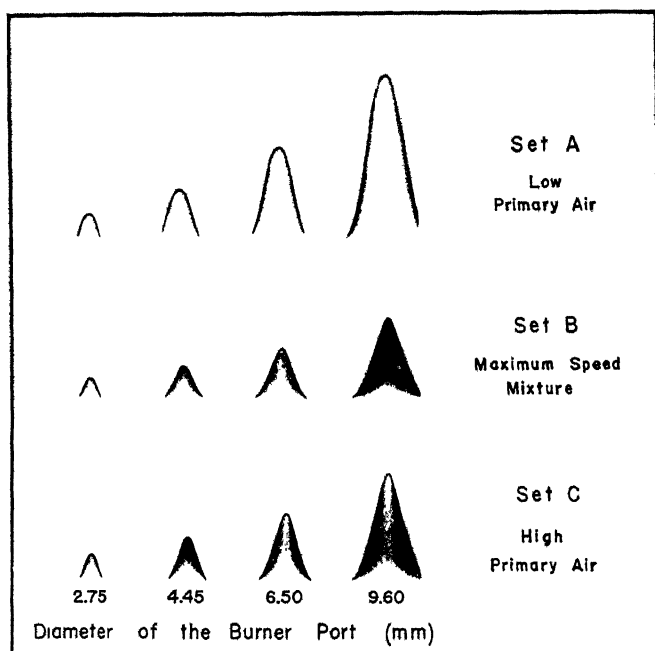


FIG. 4. Relative sizes and shapes of flames on four burners of different diameters when temperature, pressure, composition, and  $S_M$  were kept constant within each set.

Figure 5 shows the same flames with the four burners of each set enlarged by the proper amount to give each burner port the same apparent diameter. The position of the port with respect to the flame is indicated by the horizontal line under each flame. Since the composition and temperature of the mixture were kept constant, the product  $S_M \sin \alpha$  is fixed within each set. In addition  $S_M$  was also kept constant, thus concentrating any differences between flames of different size in the angle  $\alpha$ .

Table 2 shows that for the three larger burners in sets B and C the angle, and consequently the flame speed, is practically constant and independent of the size of the port.



Likewise, keeping all conditions constant except port size, any differences resulting from ports of different sizes are concentrated in the areas of the flame surfaces. Such differences are obvious in figure 5, especially in the case of set A and the smallest burner of all three sets.

Table 3 presents the enlarged areas,<sup>3</sup> measured by the method described by Corsiglia. These show clearly that the area is not independent of the size of the port. Consequently, the flame speed, computed from the volumetric rate and the actual area of the flame surface, is dependent on the size of the port.

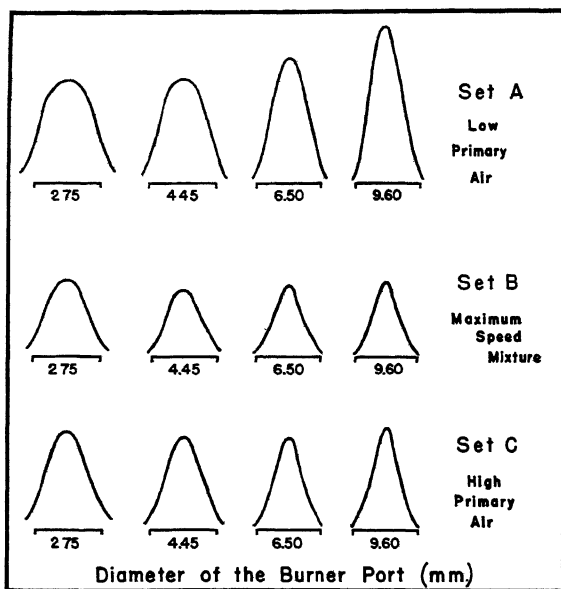


FIG. 5. Effect of burners of different sizes on the shape of the flame surface. Tracings of the flames of figure 4 with the four burners of each set enlarged by different amounts to give each burner port the same apparent diameter, the position of which with respect to the flame is indicated by the horizontal lines under the flames.

### 3. Computations of flame speed. Angle measurements versus area measurements

Table 4 shows the results of computing the flame speed, in these two ways, from measurements of the same flames. On the basis of our assumption of a definite fixed flame speed corresponding to a fixed composition and temperature of the combustible mixture, the results based on the angle appear to be a more reliable index to flame speed than those based on

<sup>3</sup> See footnote to table 3.

the area, for the case of burners larger than about 4 mm. in diameter and at or near the maximum-speed mixture. The values from the area are lower than, and appear to approach, those from the angle, and might reach coincidence if a burner of larger size were used. This is indicated in figure 3, which also shows that at about 67 per cent of the total air required the results based on the area are independent of port size, and agree with that from the angle with the 9.60-mm. burner. Whether any significance may be attached to this must await results by some such

TABLE 2

*Effect of changes of port diameter upon the angle  $\alpha$ , and consequently upon the numerical value of flame speed as calculated from measurements of the angle*

PORT DIAMETER	COMPOSITION OF MIXTURE, PER CENT PRIMARY AIR	VELOCITY OF MIXTURE, $S_M$	ANGLE $\alpha$	FLAME SPEED $S_M \sin \alpha$
Set A. Low primary air				
<i>mm.</i>	<i>per cent</i>	<i>cm per second</i>		<i>cm. per second</i>
2.75	62.3	85.4	19° 5'	27.9
4.45	62.3	85.2	16° 32'	24.2
6.50	62.0	85.1	11° 48'	17.4
9.60	61.9	85.2	9° 43'	14.4
Set B. Maximum-speed mixture				
2.75	90.4	121.0	22° 58'	47.2
4.45	89.6	120.2	26° 27'	53.5
6.50	89.6	120.4	26° 19'	53.4
9.60	89.6	120.7	26° 36'	53.7
Set C. High primary air				
2.75	103.2	140.2	19° 4'	45.8
4.45	103.5	140.0	20° 8'	48.2
6.50	100.7	140.8	20° 13'	48.7
9.60	103.7	140.3	20° 3'	48.1

method as that described by Fiock and Marvin (6) in another part of this symposium.

Such differences as are significant in the shape of the flame surface when the same mixture is burned on burners of different size and when different mixtures are burned on the same burner have long been noted and are brought out in figure 4. Measurements indicate that the base of the flame is, in most cases, about 1.0 mm. larger in diameter than the port and somewhat above it. This, on a burner of 2.75-mm. diameter, amounts to 36 per cent of the port diameter.

The incongruity between the base of the flame and the port and the

rounding off of the top of the flame lead to an area larger than that of a geometrical cone having the port as a base. Consequently, the numerical result for flame speed is lower as the distortion in shape becomes greater.

The angle is apparently affected much less than the area by the relative changes of shape and size which accompany changes in the size of the port.

TABLE 3

*Effect of changes in port diameter upon the area of the flame surface, and consequently upon the numerical value of flame speed calculated from measurements of the area.*

*Composition of  $S_M$  constant in a given set*

PORT DIAMETER	ENLARGED AREA*	FLAME SPEED VOLUME RATE/ACTUAL AREA
Set A. Low primary air		
<i>mm.</i>		<i>cm. per second</i>
2.75	654.0	18.5
4.45	729.3	16.8
6.50	801.9	15.1
9.60	869.9	13.8
Set B. Maximum-speed mixture		
2.75	589.6	29.0
4.45	455.3	38.0
6.50	390.1	43.8
9.60	356.1	47.7
Set C. High primary air		
2.75	644.4	30.7
4.45	560.9	35.9
6.50	483.7	41.3
9.60	453.8	43.6

\* The enlarged area is the area of the flame surface, in arbitrary units, measured after the flames have been brought to a common basis for comparison, by enlargement of all ports to the same apparent diameter. If changing the size of the port had no effect upon the shape of the flame, and if the flame base was congruent with the port, all four areas within a given set would be equal.

#### 4. Maximum-speed mixtures give minimum errors and are least objectionable for comparisons between fuel gases

It is clearly seen from figure 5 that the shape of the flames which yielded results least affected by changes in the size of the burner was that which departed least from the shape of a geometrical cone. This condition is found in or near maximum-speed mixtures and with the larger burners.

If the ability to measure the speed of flame relative to a combustible

mixture is to be of any use whatever, one must be able to compare the speed in one mixture with that in another, and the speeds in mixtures of one fuel gas with those in mixtures of another. The limitations of the burner method of measuring flame speeds in regard to the former have just been considered.

A problem common to all methods is that of finding a suitable basis on which to make the comparison with respect to different fuel gases. For example, the data from the two gases may be obtained by the same method, with the same apparatus, and the comparison may be made (a) by sub-

TABLE 4

*Effect on the numerical value for flame speed of computations based on measurements of the angle, as compared with those based on measurements of the area, with changes of port diameter. Composition and  $S_M$  constant in a given set*

PORT DIAMETER	FLAME SPEED $S_M \sin \alpha$	FLAME SPEED VOLUME RATE/ACTUAL AREA
Set A. Low primary air		
<i>mm.</i>	<i>cm. per second</i>	<i>cm. per second</i>
2.75	27.9	18.5
4.45	24.2	16.8
6.50	17.4	15.1
9.60	14.4	13.8
Set B. Maximum-speed mixture		
2.75	47.2	29.0
4.45	53.5	38.0
6.50	53.4	43.8
9.60	53.6	47.7
Set C. High primary air		
2.75	45.8	30.7
4.45	48.2	35.9
6.50	48.7	41.3
9.60	48.1	43.6

stituting one combustible gas for the other in a gas-air mixture which is otherwise unchanged in composition and temperature. The two gases may be methane and propane, each constituting 7.5 per cent of its mixture with air. An examination of the curves plotted in figure 6 shows that all that can be elicited from such a comparison is that the flame velocity in a very lean mixture containing 7.5 per cent of methane is more than twice that in a very rich mixture containing 7.5 per cent of propane. The comparison may also be made (b) between mixtures, each of which contains the same percentage of the total air required for the complete combustion

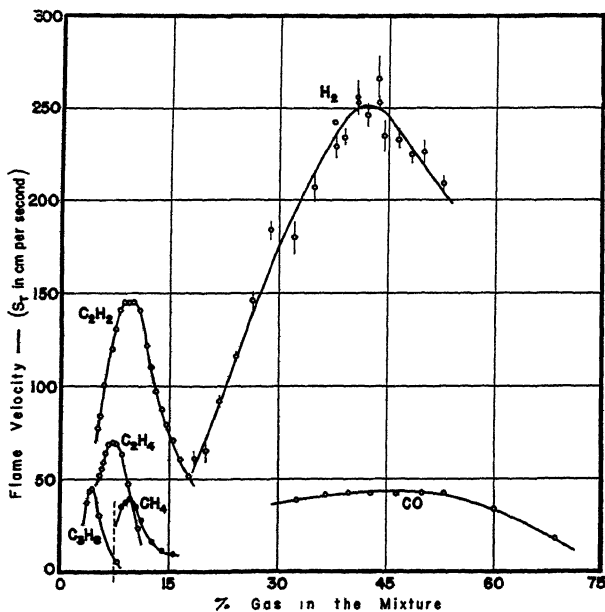


FIG. 6. Flame-speed curves plotted, in the customary manner, with "percentage of gas in the mixture" as abscissa

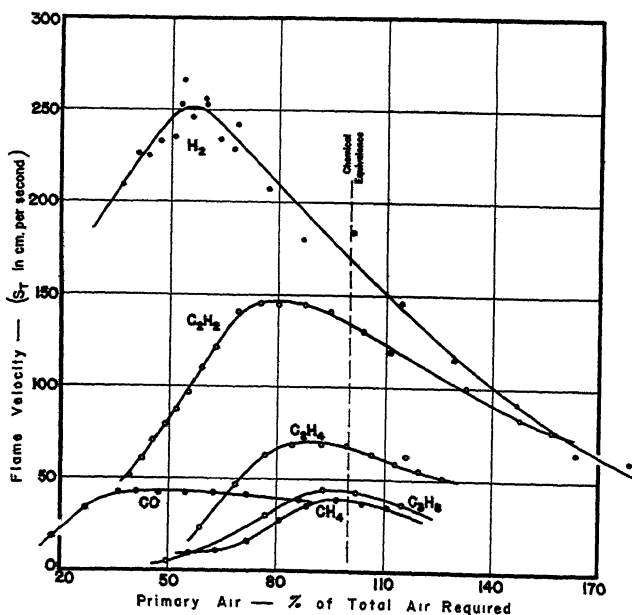


FIG. 7. Flame-speed curves plotted to place the gases on a common basis with respect to the air required for combustion, and nearly so with respect to heating value

of the respective gases. The curves plotted in figure 7 show that such a comparison may be valid between methane and propane, but if either of the gases is compared with hydrogen in mixtures containing, for example, 80 per cent of the air required for complete combustion, the same difficulties are encountered as before but not to such an extreme degree. Such comparisons are obviously useless, and the alternative of choosing the maximum-speed mixtures as the only points on the curves which are much more than roughly comparable one with another must be accepted. Even with maximum-speed mixtures, the flame speeds in different mixtures, obtained by different methods, may be compared with validity only when the different methods have been shown to yield the same result with a given mixture, the composition, temperature, and pressure being the same in each case.

*C. Changes in the distribution of velocities in a stream of mixture emerging from a burner tube*

Among the factors which influence the shape of the flame surface is the velocity of flow of the mixture. The surface of the flame may be considered to be generated by the movement of a flame front radially from a point of ignition on the outer boundary of the moving stream of mixture. If the velocity of the stream were uniform throughout, the flame front would be the surface of a segment of a sphere, all parts of which were being carried away from the burner port by the stream of mixture. If flame front and mixture traveled at the same speed, a nearly flat flame surface across the port would soon result. The spherical flame front would remain in contact with the port rim, at the original position of the point of ignition, its radius of curvature continually increasing as its center (the point of ignition) receded in the moving stream. Such a situation would probably be not far from the original conception of Bunsen, who assumed that the flame speed just exceeded the mixture velocity when the flame traveled down through the port. Although it may be approached with ports about 4 mm. in diameter or less at low rates of flow, this condition is never found in practice.

Theoretically, the distribution of velocities in a fluid in laminar flow in a tube is parabolic. This means that the maximum velocity at the axis is twice the average velocity, and that the average velocity occurs in a cylindrical lamina having a diameter 0.707 that of the tube. Ordinarily, the distribution is probably only approximately parabolic and the average velocity of the mixture is several times as great as the flame speed.

Some early workers in the field attempted to compute the changes in velocity in the various parts of such a stream of gas when it emerged from the tube into the surrounding air, but without success. They, and most

others, have assumed that the parabolic distribution persists, without significant modification, for a sufficient distance from the port to include the inner cone of the flame.

In the course of the study of flames and burners at the National Bureau of Standards, interest in this matter was revived late in 1935 in an attempt to account for the marked rounding off of the tops of some of the flames which have just been discussed. Other widely scattered workers have also become interested.

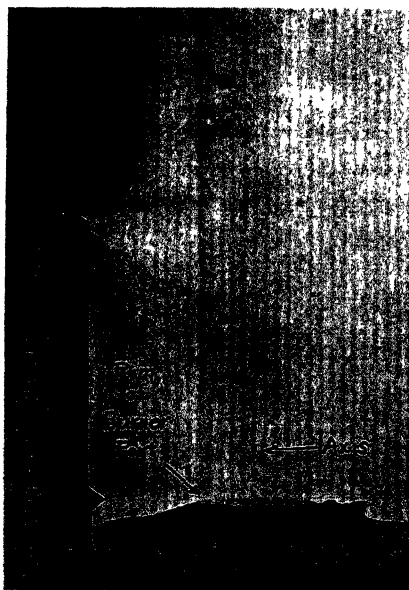


FIG. 8. Aluminum particles, suspended in a stream of air rising from a burner tube, photographed by reflected light, interrupted by a slotted disc rotating at known speed.

Some preliminary work has been done by the writer in an attempt to detect and measure such a redistribution of velocities in the stream of the mixture by photographing particles of aluminum suspended in the stream. Figure 8 shows a photograph, measurements of which indicate that there is a deceleration of particles near the axis and an acceleration of those near the boundaries of the stream. The velocity at points from 1 to 2.5 diameters above the port and near the axis was decreasing about 3.4 cm. per second in 1 cm. At the same time the velocity at points from  $\frac{1}{3}$  to 2 diameters above the port and near the boundaries of the stream was increasing about 11 cm. per second in 1 cm. on one side and from 8 to 50 cm. per

second in 1 cm. on the other. Of course, the velocity at the boundaries was still only a fraction of that near the axis at these short distances from the port, but the measurements indicate that changes of considerable magnitude in the distribution of velocity were taking place within a relatively short distance from the port.

Predvoditelev and Stupotshenko (11) have studied the problem of a decaying gas jet with pipes 100 mm. in diameter and larger by means of an anemometer. Predvoditelev (10) concludes that: "The inner cone of the Bunsen flame is a photograph of the hydrodynamic law of the distribution of velocities over the cross-section of the torch, nothing more." It seems certain that this is an overstatement of the case. Apparently he considers that the flame surface is farther from the port at the axis than it is at the boundaries of the stream, only because the velocity of flow of the mixture is greater at the axis than at the boundary. Smith and Pickering (12), as well as various other workers, have shown that the angle between flame surface and axis depends on the ratio of flame speed to mixture velocity, and not on mixture velocity alone.

### III. PROBLEMS OF STATIONARY FLAMES AS RELATED TO BURNERS

#### *A. Kinds of stationary flames*

A stationary flame may be defined as one in which a stream of combustible material flows through a flame front maintained in a fixed position by some mechanical device usually called a burner.

Stationary flames may be classified in various ways, but for the purposes of this discussion the classification will be on the basis of whether or not part of the air required for combustion of the gas is mixed with it before it emerges from the port.

#### 1. Diffusion flames

In this classification fall all those flames in which the fuel gas emerges from the burner and burns as and when it becomes mixed with a sufficient quantity of surrounding air. Such flames range from candle, wick lamp, gasoline flare, through the old gas light, the acetylene flashing beacon, some newer industrial equipment, to the old jewelers' blowpipe and modern blast lamp.

In all these the process of liberating heat is limited in speed by the rate at which mixing takes place between the gas and air. In some it is accomplished by diffusion alone. In some, mechanical mixing plays a relatively important part. In blowpipe and blast lamp mixing is accelerated by forcing a jet of air through the emerging gas. This not only increases the area of contact between gas and air, but produces considerable mixing by turbulence as well.



Such flames occupy a relatively large space compared to the rate at which they liberate heat, for the flame surface must extend itself until all the fuel gas has made contact with the air required to burn it.

## 2. Bunsen-type flames

To this class belong flames of almost all domestic gas appliances, many laboratory burners, many industrial and special-purpose burners, blow torches, welding torches, etc., in which the fuel gas is mixed with a part or all of the air it requires for combustion before it emerges from the port. Many of these burners use part of the energy of the gas supplied to them under pressure to inject or inspirate this primary air and assist in the mixing. Others have both gas and air supplied under pressure, and the mixture is controlled by means of valves.

In all these cases, however, the speed of the combustion process is limited by the speed at which flame travels relative to the particular mixture flowing from the port. It is with this class of flames that this discussion is primarily concerned.

### *B. Usefulness of flames as related to stability*

A flame is useful only so long as it remains on the burner. One may use the burner as a handle with which to change the size, direction, or intensity of the flame. Since usefulness depends on the flame remaining stable, subject to control by means of a burner under a variety of changes, problems of stationary flames are involved inextricably with those of burners.

The limits of the stable range of operation of a flame are evidenced by the flame flashing back inside the port at one extreme and being blown off the port by the stream of mixture at the other. Whether the flame operates near one of these limits or the other depends on the relative magnitudes of the flame speed,  $S_f$ , and the velocity of flow of the mixture under the varied conditions of use.

#### 1. Range of variation of velocity of mixture of constant flame speed

When the proportions of fuel and air must be kept constant while the rate of heat production is varied, as is sometimes the case, the range of stable operation with a given burner is greatest when the proportion of primary air is least. As may be seen from figure 9, for the case of a burner port 6.50 mm. in diameter burning city gas, mixtures containing less than 40 per cent of the air required for complete combustion of the gas are not likely to flash back until flow practically ceases. Likewise, a very rapid flow is required to blow the flame from the port. In the maximum-speed mixture, the range of stable operation between flash-back and blow-off is

very much less, and, in mixtures containing as much as 150 per cent of the theoretically required air, one limit or the other is encountered if only a slight variation in the rate of heating is permitted. Furthermore, the rate of heating has become so low as to be of little use. If the conditions of operation are such that the products of combustion, in escaping, exclude secondary air, the curve representing the blow-off limit doubles back toward the flash-back limit. The range of stable operation is then greatest in the maximum-speed mixture and decreases rapidly as the proportion

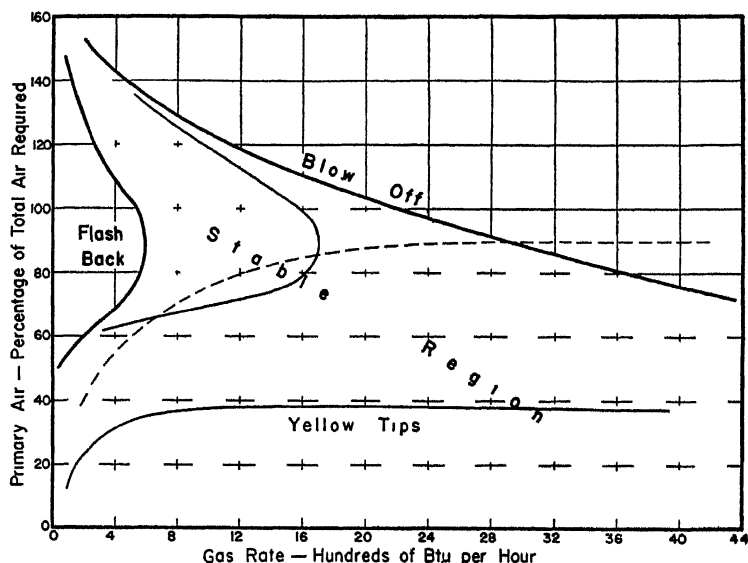


FIG. 9. Typical operation curves bounding the regions in which flash-back, blow-off, and yellow tips occur. The recurved blow-off curve results if secondary air is excluded. The dotted curve typifies the proportion of air injected by the gas. (6.50-mm. burner with city gas-air.)

of air is changed in either direction, with simultaneous reduction in the rate of heating.

## 2. Range of variations in composition

In most applications of gas flames the composition, as well as the velocity of the mixture, is subject to variation. Starting with a yellow flame, adding air to the mixture increases the flame speed and also the velocity of flow. Increasing flame speed tends toward flash-back. Increasing mixture velocity tends toward blow-off. With further addition of air stable operation continues with both limits rapidly approaching each other. If the velocity is high enough, no flash-back results, even with the maxi-

mum-speed mixture, and the tendency toward flash-back recedes with the decreasing flame speed as the addition of air continues. The increasing velocities of flow, however, soon blow the flame from the port.

If secondary air be excluded, the primary cone alone remains, as in the case of the Smithell's flame separator. The mantle flame around the port rim ordinarily seals the primary cone to the port, but when it is absent it is evident from figure 9 that mixtures near maximum flame speed are required to offset the tendency for the velocity of flow to carry the flame off the port.

For maximum usefulness it is obviously desirable to have as large as possible the range of stable operation in respect to rate of flow and composition of the mixture. The effect of the secondary combustion in keeping the flame on the port when the flame speed is low points to the mode of operation of the many "flame-retaining" devices, all of which operate on this principle.

A supplementary port (or ports) around the rim of the burner port is supplied with part of the same mixture at a lower rate of flow, or with a separately controlled mixture of constant composition and velocity, to supplement the mantle flame in maintaining a source of ignition at the port rim. Devices of the former type tested by the writer prevented the blowing off of the flame until the proportion of air in the mixture had reached around 200 per cent of that theoretically required to burn the gas. A device of the latter type will, of course, prevent blowing off entirely, and will burn at least a part of the mixture passing the main burner port even though it be well below the lower inflammable limit.

### 3. Effect of temperature of burner on stability

With many burners operating properly below 100° or 200°C. on a mixture of relatively low flame speed, the flame is blown off the port if the burner is heated to 300° or 400°C. The flame speed increases with increasing temperature, but the volume of the mixture, and consequently its velocity, are increased so much more than the flame speed that blow-off results. With burners operating properly in a higher range of temperature, or with mixtures of relatively high flame speed in the lower range of temperature (mixtures with oxygen instead of air), the temperature coefficient of the flame speed may be greater than that of the velocity of the mixture, and flash-back may result.

#### *C. Utilization of heat from flames*

The heat from stationary flames is usually utilized in one of two ways. Either the heat is absorbed and converted at relatively low temperatures,

or it is required to raise the body to which heat is being transferred to a high temperature. The flow calorimeter affords an excellent example of the efficient absorption of heat on a large surface kept at a low temperature. An example of the second case is a thermocouple formerly used in attempts to determine the temperature of a flame; the temperature attained by the junction rises until the rate of heat loss from the junction equals the rate at which heat is being supplied to it.

A body receives heat from a flame partly by radiation but mainly by conduction from the hot gases. The rate at which heat is transferred, therefore, is affected by the thermal conductivity of the layer of gases at the surface of the body, and, consequently, depends on the relative proportions of hydrogen, carbon dioxide, water vapor, carbon monoxide, nitrogen, oxygen, and other gases present in the layer in which the transfer takes place. The gases are enumerated in the order in which their effect is of decreasing importance.

If the body is a thermojunction which is small as compared to that part of the flame where the gases are hottest, there is little if any heat carried away from the junction by gases of lower temperature. Heat is lost by conduction through the leads from the junction in relation to their size and temperature, and by radiation from the junction and adjacent leads at a rate depending on their surface area and temperature. Small size of the body to be heated is a prime requisite if its temperature is even to approach that of the gases of the flame.

It is obvious that, in any specific case, the temperature attained by a body of appreciable size in a flame has little or no relation to the "flame temperature" as determined by usual optical methods.

### 1. Matching the flame to the requirements of the application

In selecting a flame for a specific purpose and keeping in mind the points just mentioned, it is usually possible to come to some decision as to the rate at which heat is to be liberated, the fuel gas to be used, the proportion of air or oxygen with which it is to be mixed, the area over which the heat is to be distributed, whether the mixture is to be variable or fixed, and, if fixed, at what composition. Access of secondary air to the flame, the space in which combustion is to take place, and whether transfer of heat by radiation from flame or refractory, or by contact with hot gases alone, is suitable, are important in making some of these decisions. Some of the various compromises involved in the case of domestic gas appliances are discussed in a circular of the Bureau of Standards.<sup>4</sup>

<sup>4</sup> C 394, section VII.

## 2. Matching the burner to the flame

There is a somewhat more definite basis for the selection of a suitable burner for a given flame than there is for the selection of the flame for a special purpose. In the interest of stability one would attempt to select a burner with which normal operation is as remote as practicable from both flash-back and blow-off.

Having decided upon the identity of the fuel gas and whether it is to be burned with air or oxygen, the range of variation of composition of the mixture permits the estimation of the range of volumetric rate of flow and the range of flame speeds involved. Values of the latter should, of course, be relative to the mixture, and not taken from the literature indiscriminately.

The relationship between flame speed and average mixture velocity within the limits of stable operation has not been fully investigated as yet. There appears to be no general relation which holds for more than two or three fuel gases in a group, or for burners of different sizes. So far, however,  $S_M$  has always been found greater than  $S_T$ . With mixtures of city gas and air and a 9.6-mm. burner, for example,  $S_M/S_T$  = about 3 at flash-back. With mixtures of hydrogen and air and a 3.8-mm. burner  $S_M/S_T$  = 1.8. At blow-off, with city gas-, carbon monoxide-, and propane-air mixtures and the 9.6-mm. burner,  $S_M/S_T$  = about 10.

By taking a value for the flame speed and the ratio of  $S_M/S_T$  in the mid range (about 6 or 7), an approximate value of  $S_M$  can be obtained. From this value and the volumetric rate a tentative diameter for the burner tube may be selected. If a computation of the Reynolds number,  $R$  (see footnote 2), indicates that the flow is turbulent, the stable range between flash-back and blow-off will be less and the applicable ratios of  $S_M/S_T$  will be different.

Studies of the effect of the depth of the port, reported by Eiseman and Smith (5), indicate that maximum susceptibility to flash-back occurs when the length (or depth) of the cylindrical port is about one-half the diameter, and that increasing the depth decreases susceptibility to both flash-back and blow-off. Turbulent flow was found to produce a marked increase in susceptibility to flash-back, other conditions remaining constant.

Of course, appropriate modifications in the above computations would be necessary in the case of a burner having multiple ports or other characteristics significantly different from a single smooth cylindrical tube.

## 3. Intensity of combustion

It has been indicated in section III C of this paper that "flame temperature" is not a reliable guide to the relative ability of different fuel gases to

heat an object to a high temperature. The maximum flame temperatures of the various gases do not differ very much, but only a few can be used for such operations as welding.

Similarly, the heating value of the fuel gas is no indication of its ability in this respect. For example, the comparison between hydrogen, carbon monoxide, and natural gas shows hydrogen and carbon monoxide to be similar with respect to the heat produced from a cubic foot, and carbon monoxide and natural gas to be about equally poor for use with torches to produce high local temperatures, while the heating value of natural gas is from three to five times that of carbon monoxide or hydrogen. Hydrogen, with the low heating value, is the only one of the three which is suitable for such uses.

TABLE 5  
*Relative combustion intensities of several fuel gases*

FUEL GAS	NET HEATING VALUE	HEATING VALUE OF MAXIMUM $S_T$ MIXTURE	MAXIMUM FLAME SPEED	COMBUSTION INTENSITY
	<i>B.t.u. per cu. ft.</i>	<i>B.t.u. per cu. ft.</i>	<i>ft. per sec.</i>	<i>B.t.u. per sec. per sq. ft.</i>
$\text{CH}_4$ .....	895	89	1.1	98
$\text{C}_2\text{H}_6$ .....	1607	95	1.4	133
$\text{C}_2\text{H}_4$ .....	1473	106	2.5	265
$\text{C}_2\text{H}_2$ .....	1414	135	4.7	634
CO .....	315	143	1.4	200
$\text{H}_2$ .....	269	117	8.8	1030

Passauer (9) and Brückner and Jahn (2) have pointed out that the maximum intensity of combustion should be attained with the maximum-speed mixture, because under these conditions the maximum quantity of heat per second can be liberated in the smallest space. The advantage of this situation in producing high local temperatures is easily seen when one considers that the smaller the area through which the heat escapes, the higher is the temperature gradient required to maintain the flow of heat at a given rate, and, consequently, the higher the temperature attained within the space where the heat is liberated.

Table 5 compares the combustion intensities of five fuel gases. Heating value and flame temperature are poor criteria by which to compare fuel gases for torch work, because, as heating value increases, so also does the quantity of air or oxygen required for combustion. The heating value of the theoretical mixture of many gases is not far from 100 B.t.u. per cubic foot. The maximum-speed mixture differs from the theoretical by varying amounts for the different gases, and the heating value of the former is

slightly the higher. The mixture with which maximum flame temperature is attained is not far from the maximum-speed mixture. The heating value for these mixtures is of the same order of magnitude for all the gases, thus accounting for the similarity of the "flame temperatures."

The maximum flame speed is thus left as the significant and controlling factor in determining the intensity of combustion. The means by which intensity can be controlled are those which affect flame speed. The substitution of premixed primary air for diffusion processes with secondary air, of ethylene, acetylene, or hydrogen for carbon monoxide or the paraffin hydrocarbons, of oxygen for air in the mixture, and preheating the mixture, all increase flame speed and intensity of combustion.

#### *D. Turbulence, flame speed, and noise*

Scattered through the literature are numerous statements, often conflicting, concerning the interrelationships between turbulent flow, flame speed, and noise. It seems very improbable that turbulence would have any effect on the speed of the flame relative to the mixture, but it does increase the mass rate of burning by increasing the area of the flame surface.

Probably the most exhaustive and careful study of these problems has been Project No. 13 of the Committee on Industrial Gas Research of the American Gas Association (1). This work shows without question that, in general, noise increases with the velocity of flow of the mixture and with the flame speed, and that no noise results when a homogeneous mixture emerges from the ports in laminar flow. (In the latter case the flame front is at rest.)

Of course, in excess of the critical velocity, turbulence increases as the velocity of the mixture increases. Thus, increasing noise may result from a simultaneous increase in turbulence and in flame speed, which might then be associated by the unwary as cause and effect. It is more probable that the flame speed is fixed by the properties of the mixture, regardless of the vagaries of motion of the medium in which the flame travels.

There is little doubt that the source of the sound is in the random disorganized changes of position of the flame front. The part of the flame which is most active depends on individual circumstances. It may be the flickering at the base, caused by intermittent blow-off, which can be remedied by the use of any means which keeps the flame seated on the port. It may be the entire flame surface in a jumble of random incipient flash-back and blow-off, in a multiplicity of explosions of small masses of mixture partially detached from the stream and ignited separately.

In some cases, like those reported by Eiseman and Smith (5), there might be some reason to suspect that the noise was the result of resonance

in the burner. The sound, at times, approached a pure note, the pitch and loudness of which increased with flame speed and rate of flow. The flame surfaces could be observed in rapid alternation between two sharply defined positions. The sound was absent, however, when the mixture, otherwise unchanged in any way, was allowed to flow without ignition.

#### IV. SUMMARY AND CONCLUSIONS

Numerical values for flame speeds obtained with burners are affected by the various ways in which the measurements of the flames are made, by experimental conditions, and by the different ways in which the results are computed.

Measurements of the angle between flame surface and axis at a point  $0.7r$  from the axis, on flames resulting from mixtures in laminar flow at or near the composition for maximum flame speed and on burners over 4 mm. in diameter, yield results least affected by variations in experimental conditions.

Maximum flame speeds alone are suitable for making comparisons between different fuel gases because of the lack of any common basis (in point of composition) for comparison.

An appreciable redistribution of velocities in the stream of the mixture takes place as the stream leaves the port. This takes the form of an acceleration near the boundaries of the stream and a deceleration near the axis, and affects the shape of the flame surface.

Although burner methods of measuring flame speed are relatively simple and the results directly applicable to a multitude of burner problems, the field of usefulness of the method appears at present to be considerably restricted by the limitations mentioned above.

The usefulness of flames is dependent on their stability and susceptibility to control. Laminar flow, favored by deep ports and small diameters of the port, increases the range of stable operation between the limits of flash-back and blow-off. Complete mixing and low proportions of air do likewise. Such conditions also tend to eliminate turbulence and noise.

In the absence of secondary air, the maximum range of stable operation is found with the maximum-speed mixture. The range is about half that in secondary air, and decreases rapidly as the composition of the mixture is changed in either direction.

In selecting a flame for a definite purpose one should keep in mind the fact that the temperature attained by the body being heated rises until the rate at which heat is lost becomes equal to the rate at which it is supplied.

In choosing the dimensions of a burner for a given flame, a likely value for the average velocity of flow of maximum-speed mixtures with air will be from six to seven times the maximum flame speed.



Where local high temperatures are required, they can be obtained by providing conditions which result in the liberation of heat at the highest rate in a given space. Maximum flame speed rather than flame temperature or heating value of the gas is the key to this. The heating value of the maximum-speed mixture, multiplied by the maximum flame speed, is an index to intensity of combustion (B.t.u. per second per unit area).

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# COMPARISON OF IDEAL AND ACTUAL COMBUSTION TEMPERATURES AND PRESSURES: ANOMALOUS EFFECTS; GAS VIBRATIONS<sup>1</sup>

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The calculation of flame temperatures, expansion ratios of flames, and explosion pressures for the case of ideal, i.e., complete and adiabatic, combustion, involves the solution of a number of equations, which may be divided into three groups. One equation represents the energy balance of the system; that is, the energy released in the chemical reaction equals the thermal energy gained by the system. The second group comprises several equations describing the material balance of the system, one equation for each atomic species participating in the reaction. The third group comprises the dissociation constants of the chemical equilibria involved. The solution of the equations is a somewhat involved procedure, but it presents no fundamental difficulties. The calculations can be made accurately by the use of energy contents and equilibrium data determined from band spectroscopy (7).

In explosions in closed vessels with local ignition one must also take into consideration the effect of the temperature gradient in the vessel at the end of the explosion on the pressure developed. This has been discussed elsewhere, and it has been shown that the temperature gradient lowers the pressure a few tenths of a per cent, depending on the mixture composition (8).

To approach as closely as possible to adiabatic combustion the flame gases should not be in contact with cooling surfaces. In closed-vessel explosions this condition is most nearly realized in spherical vessels with central ignition. The flame is insulated from the wall by a layer of un-

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burnt gas up to the point of maximum pressure. It is, however, unavoidably in contact with the ignition rod. One may minimize heat loss by making the latter as small in diameter as possible and choosing a reasonably large vessel, avoiding, as far as possible, deviations from the spherical contour of the vessel. Radiation loss could be reduced by polishing the wall, but it appears that possibly only in slow carbon monoxide explosions is the thermal radiation of carbon dioxide not negligible.

Table 1 contains a summary of comparisons between ideal and experimental explosion pressures for hydrogen-oxygen explosions (9). The explosion pressures were observed by a number of investigators,—Pier, Bjerrum, Wohl and Magat, and Lewis and von Elbe.

In explosions (a) excellent agreement is obtained between experimental and calculated pressures, indicating that within the limits of accuracy of

TABLE 1  
*Average percentage deviation of observed from calculated explosion pressures for hydrogen-oxygen mixtures containing different inert gases*

TYPE OF MIXTURE	NUMBER OF EXPLOSIONS	AVERAGE PERCENTAGE DEVIATION OF OBSERVED FROM CALCULATED PRESSURES
(a) ( $H_2$ , $O_2$ ) + small excess of $H_2$ + A + $H_2O$ . . . . .	15	+0.07
(b) ( $H_2$ , $O_2$ ) + large excess of $H_2$ + $H_2O$ . . . . .	11	-0.61
(c) ( $H_2$ , $O_2$ ) + large excess of $H_2$ ; dried with $P_2O_5$ . . . . .	10	-2.00
(d) ( $H_2$ , $O_2$ ) + excess $O_2$ + $H_2O$ . . . . .	6	+1.22
( $H_2$ , $O_2$ ) + $N_2$ + $H_2O$ . . . . .	8	+0.79

measurement these explosions are ideal. The slightly low results in explosions (b) have been shown to be due to heat loss to the ignition rod, the gas containing a large excess of hydrogen and therefore being highly conductive.

Explosions (c) illustrate the results with dry hydrogen-oxygen mixtures. The observed pressures are, on the average, 2 per cent below the calculated, a discrepancy that lies outside the experimental error. When small amounts of water vapor are added to the initial mixture the discrepancy disappears except for the heat loss through the ignition rod, 1.3 mm. of water vapor being sufficient to do this. Furthermore, as shown by other experiments not included in the table, the deviations from the ideal explosion pressures decrease as the initial pressure is increased to several atmospheres. The following explanation has been proposed for the phenomenon. The discrepancy is due to loss of energy by luminescent radiation from the flame front. Highly vibrating molecules of OH or

$\text{H}_2\text{O}$  are formed in the reaction, which radiate unless quenching takes place by a collision of the second kind with appropriate molecules such as diluent unexcited  $\text{H}_2\text{O}$ . The luminescence radiation may also be quenched by increased pressure. To date, experimental confirmation of this explanation is still lacking.

In explosions (d) the observed pressures are higher than the calculated, the anomalous effect being greater in excess oxygen than in nitrogen mixtures. The effect disappears when the oxygen or nitrogen is replaced by helium or argon. The anomaly can be reasonably explained only by assuming that there is a momentary excess of translational energy at the end of the explosion. This could be the case if a time lag exists in the excitation of the vibrational energy levels in oxygen and nitrogen molecules. The energy released in the chemical reaction then flows first into those degrees of freedom that offer least hindrance. These are particularly translation and also rotation. The explanation is supported by experiments on the velocity of sound in these as well as other gases, notably carbon dioxide, carbon monoxide, nitrous oxide, and chlorine, where the existence of such an excitation lag was established.

It is noteworthy that excitation lag is not observed in explosions of ozone diluted with oxygen (9). This would indicate that the highly energized molecules of oxygen emerging from elementary reactions of decomposing ozone are capable of distributing their excess energy among all degrees of freedom of diluent oxygen molecules,—namely, molecules of their own kind,—in an extremely short period of time compared with the progress of the flame front. The process by which this energy distribution takes place may be discussed briefly. It may be assumed that vibrational quanta are readily transferred in collisions between two oxygen molecules. If the transfer takes place between two neighboring quantum states, there is perfect resonance and no interchange of translational or rotational energy with vibrational energy will occur. If, however, the transfer occurs between more remote quantum states, then, owing to the smaller energy quantum of the upper level, other forms of energy, translational and rotational, must participate in the transfer. Thus in sound velocity experiments (5) which have been carried out near room temperature and where only the first vibrational level is excited, the vibrational quantum has a long lifetime and no interchange with other forms of energy occurs. In ozone explosions the oxygen molecules are excited to various high vibrational levels, and the exchange of vibrational energy leads to interchange with other forms of energy and thus to rapid establishment of thermodynamic equilibrium.

It is of interest that ozone explosions yield a value of the electronic  $^1\Delta$  level of the oxygen molecule of  $0.85 \pm 0.1$  volt (10), compared with the

spectroscopic value of 0.97 volt (4). The closeness of the agreement is emphasized by the fact that at the highest explosion temperature, 2500°K., the difference between the observed and spectroscopic values amounts to less than 10° difference between the observed and theoretical explosion temperatures and is in the direction to be accounted for by slight heat loss during the explosion.

For carbon monoxide-oxygen explosions experiments of Pier (12) and David and Leah (2) are available. They have been compared with ideal pressures by the present authors.<sup>2</sup> Pier exploded dry and moist mixtures; David and Leah exploded mixtures containing a small percentage of hydrogen. In Pier's experiments the pressures fall generally several per cent below the calculated except for a mixture containing a large excess of carbon monoxide, where the reverse is true. Here the heat loss is presumably overshadowed by excitation lag. David and Leah's experiments show generally much smaller pressure loss. In mixtures containing a large excess of carbon monoxide the observed pressure is again larger than the calculated. That heat losses in carbon monoxide-oxygen explosions considerably exceed those in hydrogen-oxygen explosions is not surprising in view of the much longer duration of the former explosions (of the order of tenfold), which accentuates radiation loss and conduction to the ignition rod and causes early contact of the burnt gas with the wall, owing to convective rise. Concerning the differences in heat losses in Pier's and in David and Leah's experiments, it is probable that the presence of a small amount of hydrogen in carbon monoxide-oxygen mixtures shortens the combustion time more than the presence of water vapor.

Pier's (12) explosions of mixtures of acetylene and oxygen show that excitation lag is more pronounced with oxygen as diluent than with nitrogen. This agrees with the experience in the hydrogen-oxygen explosion series. Diluent carbon dioxide also shows a strong excitation lag.<sup>2</sup>

Expansion ratios have been measured by soap-bubble explosions of mixtures of carbon monoxide and oxygen diluted or not with helium or argon (3). The results show a trend similar to that found for the explosion pressures in spherical vessels. On the lean side the expansion ratios fall below the calculated considerably more than in the case of explosion pressures. Apart from radiation loss one must again consider the cooling effect of the ignition rod. The latter consisted of metal wires. Since the mass of gas used in these soap-bubble explosions was much smaller than in Pier's and in David and Leah's spherical-vessel explosions (of the order of  $\frac{1}{100}$ ), a considerably greater percentage heat loss through the ignition rod is to be expected. On the rich side the expansion ratios

<sup>2</sup> For details consult Lewis and von Elbe: *Combustion, Flames and Explosions of Gases*, Cambridge University Press, in press.

are grouped more closely around the calculated values. It is suggested that here there is a partial cancellation of heat loss by excitation lag.<sup>2</sup>

There does not seem to be any way to reconcile the very low flame temperatures measured by David (1) with a platinum-wire thermometer in the early stages of flame in a spherical vessel, with the above results. One may suspect errors in the temperature measurements. David and Leah's results discussed above are also in disagreement with these wire temperature measurements.

The sodium line-reversal method, the reliability of which has been proved by the work of Kohn (6) and others, is particularly suited for measurement of the temperature of stationary flames. Consideration of the structure of stationary flames such as Bunsen or Méker flames, points to an uncontrollable admixture of the surrounding atmosphere, particularly at the base of the cone. Therefore measurements of the temperature of such flames should be interpreted with caution. If the temperature is measured solely in some interior portion of the flame, then the protection afforded by the outer flame should suffice to bring such measurements into substantial agreement with the experience on explosion pressures and expansion ratios. This is the case. It is, however, to be borne in mind that heat losses occur to the grid of the Méker burner. These losses can be reduced by increasing the gas velocity.

Figure 1 shows some results obtained by Minkowski, Müller, and Weber-Schäfer (11) with rich coal gas-air mixtures containing an unspecified amount of water, using the line-reversal method and a protected flame. The curves are flame temperatures calculated by the present authors for dry and for water-saturated mixtures. It is noted that the experimental points fall below as well as above the theoretical curve, and that they arrange themselves according to the gas velocity. The closer the mixture is to the stoichiometric, the larger the gas velocity required to raise the temperature of a given mixture to or above the theoretical curve. This can be explained by the higher flame speed of such mixtures, which brings the burning gas closer to the grid, thus increasing the grid loss. Some values fall considerably above the theoretical curve, again pointing to excitation lag.

The results with Pittsburgh natural gas described by Kaveler and Lewis in the next paper are in harmony with the above results. Since the flame speed of natural gas is much smaller than that of coal gas, both grid losses and excitation lag are less pronounced, the latter because there is much more time for the establishment of thermodynamic equilibrium.

The excitation lag seems to be responsible for the occurrence of the peculiar gas vibrations that appear in closed-vessel explosions and that have been observed by many investigators (9) with various explosive

mixtures between certain limits of composition in vessels of various shapes and sizes. Figure 2 shows the effect in hydrogen-oxygen mixtures diluted

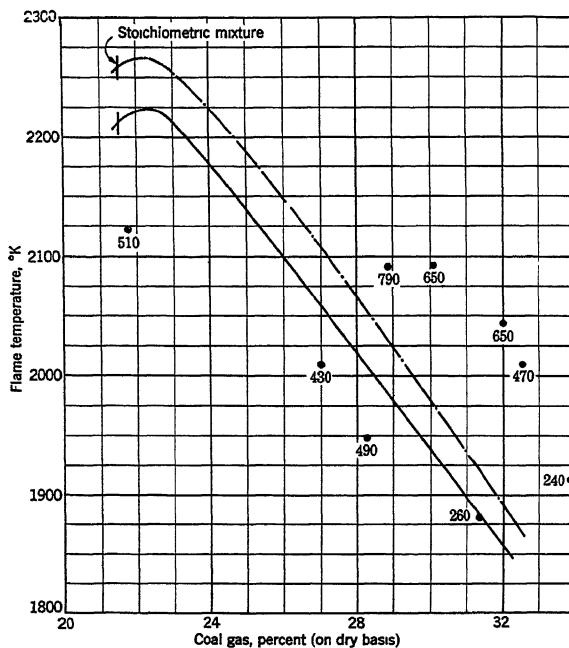


FIG. 1. Comparison of theoretical flame temperatures of coal gas-air mixtures with experimental flame temperatures determined by the line-reversal method. — · —, theoretical curve, dry mixtures; —, theoretical curve, moist mixtures; ●, sodium line-reversal flame temperatures with gas velocity in centimeters per second.

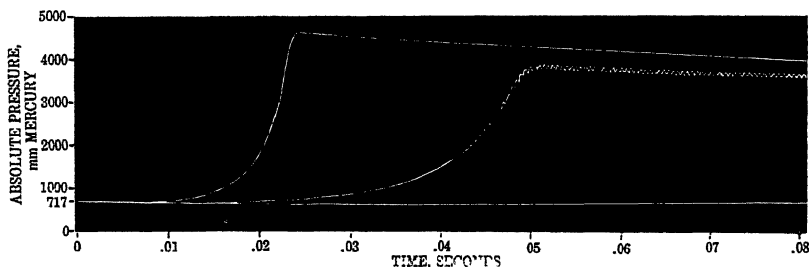


FIG. 2. Vibration effect in hydrogen-air explosions. Slower explosion, 15 per cent of hydrogen; faster explosion, 20 per cent of hydrogen.

with nitrogen. It is observed that the vibrations commence long before maximum pressure, beginning when the pressure starts to rise steeply, and that they occur only in the slower of the two explosions. With an

equal amount of oxygen as diluent, the vibrations are so intense that it is impossible to obtain a pressure record. The vibrations do not appear in mixtures containing excess hydrogen, helium, or argon. There seems to be little doubt, therefore, that they are in some way connected with the ability of the gas mixture to exhibit the excitation lag. The origin of the vibrations may be proposed as follows: Normally one expects the excitation lag to be localized in the freshly burnt gas forming a shell around the burnt core, since considerable time has elapsed since the core burned. The persistence of the excitation lag is an inverse function of the temperature, probably of an exponential character. Therefore in low-temperature explosions the chances are better that the lag persists in the deeper layers of the core. When the rate of pressure rise becomes steep, there is a steep rise in the temperature of the core, causing a rapid increase in the rate of attainment of energy equilibrium and consequently a rapid shrinkage in volume of the inner layers of gas. This results in a sudden inward mass movement of the gas which may be likened to an implosion. In this way pressure waves are set up which, because of little damping, continue for some time. The disappearance of the phenomenon on enriching the mixture may be ascribed to the higher combustion temperature which shortens the duration of the excitation lag in the inner gas layers.

#### SUMMARY

In moist hydrogen-oxygen mixtures diluted with argon, helium, or excess hydrogen, explosion pressures are found that agree with the theoretical pressures calculated from band spectroscopic data. In dry mixtures the observed pressures are lower, possibly owing to heat loss by luminescence radiation. In moist mixtures diluted with nitrogen or excess oxygen the pressures are higher. This has been ascribed to the time-dependence of specific heats, called excitation lag. This excitation lag has been linked to gas vibrations which appear early in the explosion. The results with carbon monoxide-oxygen and with acetylene-oxygen mixtures can also be interpreted by heat loss and excitation lag. If a small amount of hydrogen is added to carbon monoxide-oxygen mixtures the heat loss appears to be reduced considerably, probably owing to the shorter duration of the explosion. Excellent agreement is found between experimental and theoretical explosion pressures in ozone-oxygen mixtures. An explanation of the absence of excitation lag in the latter is proposed. Measurements of expansion ratios in soap-bubble explosions of carbon monoxide-oxygen mixtures and flame temperatures by the line-reversal method of coal gas-air mixtures show a trend similar to explosion pressures in hydrogen-oxygen and carbon monoxide-oxygen mixtures.



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# FLAME TEMPERATURES AND VERTICAL GRADIENTS IN NATURAL-GAS FLAMES<sup>1</sup>

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The purpose of the experiments described in this paper was to obtain information on the state of the burnt gas that emerges from a flame by comparing observed maximum flame temperatures determined by the sodium line-reversal method with calculated theoretical temperatures, and by investigating very carefully the nature of the temperature gradients in the vertical direction above the cones of suitably constructed stationary flames.

## EXPERIMENTAL METHOD AND PROCEDURE

The accuracy and reliability of the line-reversal method for measuring flame temperatures have been demonstrated by a number of investigators (2) and the method has become standardized. The apparatus used was essentially that employed in previous experiments in this laboratory (1). Some modifications in the details of the apparatus and procedure will be described here.

Two-stage reducing valves with surge chambers of appropriate size were employed to give a steady flow of the gases so that a very steady flame was produced. Air and/or oxygen was passed first through a sodium chloride-vaporizing chamber before entering a mixing chamber. The mixing chamber was a 500-cc. flask in which the natural gas and air or oxygen were premixed before entering the burner.

The composition of the combustible entering the burner was determined from two samples (250 cc. each) which were slowly withdrawn from the mixing chamber. A measurement of temperature gradient usually required thirty minutes, so that one sample was withdrawn during the first

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ten minutes and the other during the last ten minutes of this period. The gas was analyzed with a conventional Orsat apparatus. The per cent of oxygen was determined by absorption with pyrogallol reagent up to a concentration of 30 per cent and with chromous acetate reagent when the concentration exceeded this value. Pittsburgh natural gas in the combustible mixture was determined by combustion over a heated platinum wire, the content being determined from the sum of the contraction and carbon dioxide, using a factor determined by careful Orsat analyses of the natural gas. The accuracy of the analyses is 3 per cent or better, as determined by duplicate analyses on each sample taken.

The tungsten-band lamp used in these experiments was aged and calibrated by the manufacturer. The calibration was frequently checked during the course of the work and was found to be constant. The current through the lamp was read to 0.10 ampere, equivalent to  $\pm 5^{\circ}\text{C}$ . The reversals could be easily read to that limit even for natural gas-oxygen flames for which the reversals become more difficult to follow, owing to the low intensity of the D-radiation from these flames. This is probably due to the suppression of the sodium-atom concentration by the presence of the large excess of oxygen in the gases.

A color correction ( $+26^{\circ}\text{C}$ .) and a lens correction ( $-20^{\circ}\text{C}$ .), as explained elsewhere (1), were applied to the observed temperatures.

#### AN IMPORTANT EXPERIMENTAL REQUIREMENT

Stationary flames have both vertical and horizontal temperature gradients. The horizontal gradients arise mainly from the interdiffusion of air from the surrounding atmosphere, which causes either secondary combustion or dilution depending upon whether a rich or a lean mixture is being burned. The temperature of the sodium layer nearest the spectro-scope determines, for the most part, the temperature reading. In totally colored flames this sodium layer is greatly affected by such interdiffusion. It was desired to eliminate as far as possible this complicating effect of the horizontal temperature gradient. This could easily be accomplished by coloring only the central part of the flame, so that the temperature observations were confined to presumably isothermal horizontal sections protected from secondary air.

#### TYPE OF BURNER

In order to obtain centrally colored flames a concentric-tube burner was used. The details of the construction of this burner are shown in figure 1. The outer brass tube of the burner was threaded (40 threads per inch), so that by means of the graduated knurled nut the burner could be moved in the vertical direction.

A number of attempts were made to produce a partially colored single-cone flame over the concentric-tube burner, but the single cone was unstable and vibrated excessively, with a tendency to form a double flame consisting of a cone system on each tube. Temperature observations on partially colored flames were finally made using a nichrome grid. The grid was made from strips of metal 0.5 mm. thick forming a square mesh 2 mm. on edge over the cross section of the burner.

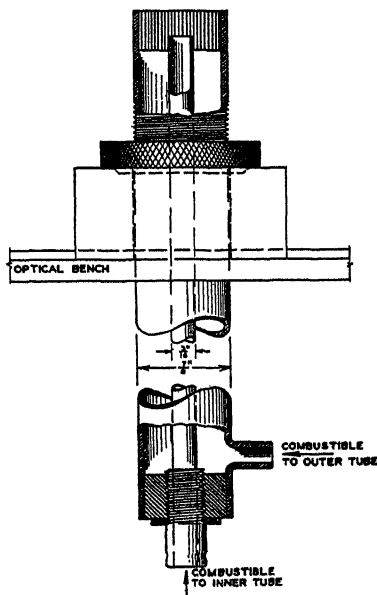


FIG. 1

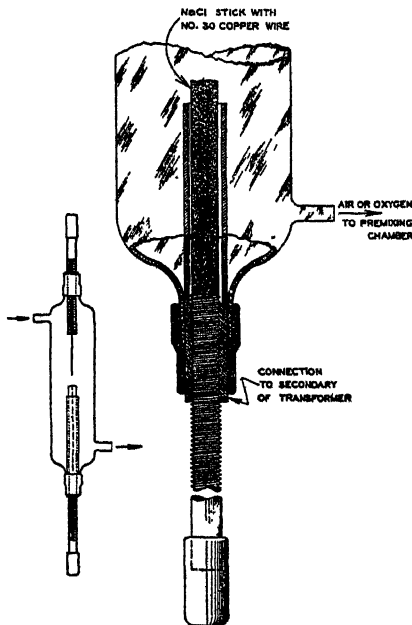


FIG. 2

FIG. 1. Concentric-tube burner for producing partially colored flames

FIG. 2. Detail of sodium chloride electrode and vaporizer

#### METHOD OF INTRODUCING SODIUM

The conventional wet method of coloring flames causes water droplets to be introduced into the combustible mixture. In order to eliminate any uncertain effects from this source, we used the following electric-arc method of introducing sodium into the combustible mixtures: A sodium chloride vaporizer, represented in figure 2, was made from a glass tube drawn down to fit brass bushings which were  $\frac{3}{8}$  in. by 1 in. and were fastened to the glass by rubber tubing. The electrodes for producing the electric arc were a No. 18 platinum wire and a stick of sodium chloride attached to bolts as shown in the figure. The stick of sodium chloride was  $\frac{1}{4}$  in. by 6

in. and was prepared by compressing moistened salt at a pressure of three or four thousand pounds per square inch in a special mold made from two machined steel blocks. The sticks were air-dried for ten days, after which they could be handled without breaking easily. A radial groove was cut down the length of each stick so that a length of No. 30 copper wire could be placed down the center of it. The copper-wire core is an essential feature of the sodium chloride electrode, for it keeps the arc directed to the center of the salt stick, whereas otherwise it would tend to follow a path in the ionized air. The sodium chloride stick was glued to the lower bolt to which one end of the copper wire was soldered. A brass-tube guide was used to keep the salt stick centered in the glass tube. A 250-watt transformer delivering 2000 volts on the secondary was used to supply energy for vaporizing the salt stick. Lower voltages were not so satisfactory for maintaining a continuous arc for long periods. It is essential that the size of the copper wire be so chosen that it will burn away at the same rate as the salt stick. The vaporizing device was operated manually. After the arc was struck, the sodium chloride was fed into the system by screwing in the lower bolt. At each setting, the stick would burn for three or four minutes, which was sufficient time for a temperature reading. The amount of salt vaporized in the stream could be easily regulated and maintained constant by varying the energy input of the transformer.

Oxygen or air was passed through the vaporizer from which the salt-laden gas passed to the mixing chamber. At the mixing chamber the gas was divided into two streams. One passed directly to the inner tube of the burner, and the other to the outer tube through a filter to remove sodium chloride dust. The filter consisted of a wad of cotton, 6 in. thick, flanged into a can 12 in. in diameter and 8 in. deep. The pressure drop through this filter was very small, and the flow through either channel was regulated by pinch clamps on the line. The procedure of premixing the gas and removing a portion of the salt vapor was necessary to insure uniformity of combustible composition in both streams.

#### COMPOSITION OF PITTSBURGH NATURAL GAS

The natural gas used in the experiments was taken from the laboratory supply and compressed to 1500 lb. in a large cylinder.

The average of six Orsat analyses of this gas was as follows: methane, 85.48 per cent; ethane, 13.85 per cent; nitrogen, 0.67 per cent. The maximum deviation from this average was 0.40 per cent. A sample of the gas was also subjected to a low-temperature fractionation, and the result was: methane, 88.6 per cent; ethane, 9.3 per cent; propane, 1.8 per cent; butane, 0.3 per cent; nitrogen, nil. Considering 0.67 per cent nitrogen (undetectable) as present in the methane fraction, this analysis is in satisfactory agreement with the Orsat analysis.

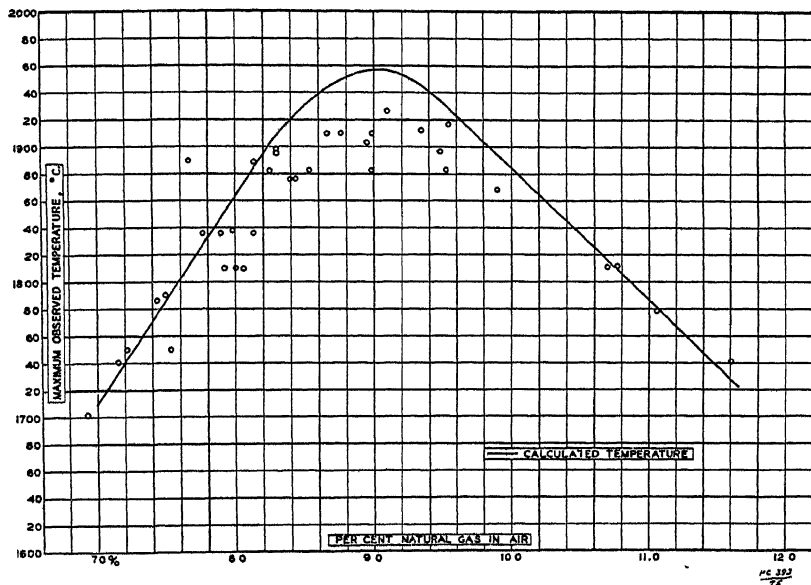


Fig. 3. Maximum observed temperatures; partially colored natural gas-air flames

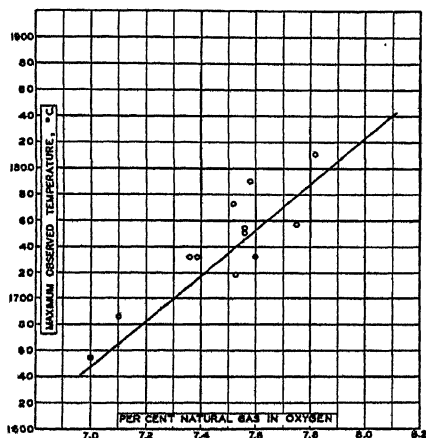


Fig. 4. Maximum observed temperatures; partially colored natural gas-oxygen flames

#### CALCULATED FLAME TEMPERATURES

The theoretical flame temperatures for Pittsburgh natural gas with air and with oxygen were calculated by the method outlined by Lewis and von Elbe (3), and are given by the curves in figures 3 and 4. The heats of

combustion used were those given by Rossini (5). The heat capacities and dissociation equilibria used for the temperature calculation were those compiled by Lewis and von Elbe (4) from spectroscopic data. The calculated temperature is but slightly changed if one expresses the composition of natural gas as methane and ethane rather than in terms of its true hydrocarbon content. This is the case since the respective heats of combustion are nearly the same per mole of water and carbon dioxide formed, and because the bulk of the gas is methane. The values are correct to within 2° to 4°C.

#### OBSERVED TEMPERATURE GRADIENTS IN FLAMES OF NATURAL GAS AND AIR

Some preliminary temperature observations were made on completely colored flames using a  $\frac{3}{8}$ -in. brass tube with a grid as the burner. The observed maximum flame temperatures agreed quite well with those previously reported from this laboratory (1). As usual with completely colored flames, the observed temperatures were higher than the calculated on the rich side and lower on the lean side. There was always a positive temperature gradient above the tips of the cones, with the maximum temperature about 5 to 6 mm. above the cones. When the nitrogen in the air was replaced by oxygen, the point of maximum temperature approached the cones, and at about 50 per cent oxygen there was no vertical gradient for 1 to 2 cm. above the cones.

The effect of coloring just the central portion of the flame is shown in table 1. The temperature of the partially colored flame is considerably higher than that of a completely colored flame of the same size. The data given for the small, completely colored flame indicate that the effect of secondary air becomes greater as the flame size is reduced. The effect of partially coloring flames for line-reversal temperature measurements, as shown in table 1 (column C), is typical of the experiments reported in this paper.

As the space velocity of the combustible mixture is increased, the gradient above the cones shifts to a higher temperature range and becomes smaller, while the maximum temperature is maintained over a greater distance. This is shown in table 2.

The positive gradient above the cones of these natural gas-air flames may be explained as arising from heat losses through the grid. Relatively cold layers of gas rise in the centrally colored stream from the base of the cones near the grid enveloping the colored stream, and give rise to an observed temperature lower than the average temperature over the cross section. Owing to mixing above the cones these cold layers disappear, and the observed temperature increases. When the space velocity is increased the grid losses are decreased (table 2).

In figure 3 the maximum observed flame temperatures for various mixtures of natural gas and air are compared with calculated theoretical flame temperatures. For lean and rich mixtures the agreement between

TABLE 1  
*Flame temperatures of completely and partially colored flames\**

HEIGHT ABOVE CONE	TEMPERATURE		
	A	B	C
mm.	°C.	°C.	°C.
-0.6	1654	1638	
0.0	1678	1694	1741
+0.6	1686	1710	1778
1.9	1710	1764	1810
3.2	1718	1790	1852
4.4			1882
6.4	1686	1824	1896
9.5	1615	1838	1896
12.7		1838	1896
15.9		1838	

A, completely colored flame over  $\frac{3}{8}$ -in. grid; B, completely colored flame over  $\frac{1}{4}$ -in. grid; C, partially colored flame over  $\frac{1}{4}$ -in. grid.

\* 8.52 per cent natural gas in air.

TABLE 2  
*Effect of space velocity on temperature gradient and maximum temperature\**

HEIGHT ABOVE CONE	°C. FOR CUBIC FEET PER SECOND THROUGH BURNER				
	0.00060	0.00094	0.00119	0.00159	0.00201
mm.					
-1.3	1654				
-0.6	1686				
0.0	1702	1718	1726	1732	1750
+0.6	1718	1718	1832	1750	1764
3.2	1732	1732	1750	1764	1778
5.4	1718	1750	1764	1778	1778
9.5	1702	1741	1750	1778	1772
12.7				1778	1764

\* 10.85 per cent natural gas in air.

observed and theoretical temperatures is very close. In the region of the maximum temperature, the observed temperatures are 20° to 40°C. below the theoretical. Table 3 permits a comparison of the temperature at the cones and the maximum observed temperature for experiments recorded in



figure 3. The temperature differences are, on the whole, smaller for the leaner mixtures. This is further evidence that heat losses are smaller for lean mixtures, as may be expected from the lower temperatures of the flames and from the greater separation of the burning zone from the grid owing to lower flame speeds.

The scattering of the experimental points in figure 3 is mainly due to the difficulty of maintaining the mixture composition constant.

TABLE 3

*Difference between temperature above the cones and maximum temperature for natural gas-air flames*

NATURAL GAS IN AIR	FLAME TEMPERATURE		DISTANCE ABOVE CONE	TEMPERATURE DIFFERENCE
	At cone	Maximum		
<i>per cent</i>	<i>°C.</i>	<i>°C.</i>	<i>mm.</i>	<i>°C.</i>
6.51	1568	1638	3	70
7.15	1650	1741	5	91
7.22	1690	1750	9	60
7.44	1742	1786	9	44
7.54	1670	1750	9	80
7.67	1786	1890	8	104
7.77	1746	1836	9	90
7.90	1746	1836	9	90
8.00	1742	1810	9	68
8.06	1766	1810	9	44
8.13	1718	1836		118
8.14	1738	1888	10	150
8.31	1778	1898	8	120
8.53	1734	1882	6	148
8.99	1776	1910	8	134
9.35	1810	1912	9	102
9.48	1766	1896	9	130
9.55	1810	1916	9	106

#### EXPERIMENTS WITH NATURAL GAS-OXYGEN MIXTURES

The maximum flame temperatures for these flames were observed immediately at the cone. Above the cone the flame temperature decreased uniformly for several centimeters from this point. Since the flame speed in oxygen mixtures is faster than in air mixtures, the space velocity in these experiments was much greater. The experimental maximum temperatures are compared with the theoretical calculated temperatures in figure 4, where it is seen that the experimental points tend to be higher than the calculated. In view of the fact that heat losses occur, the negative gradient above these flames indicates the existence of excitation lag (see

preceding paper). The latter would obscure the positive gradient arising from heat losses, since these are smaller in oxygen flames owing to the high space velocity.

#### SUMMARY

Flame temperatures were measured by the sodium line-reversal method along the vertical axis of centrally (partially) colored Méker flames for mixtures of natural gas with air and oxygen. For air mixtures the vertical temperature gradient above the cones is positive. The temperature range and length of the positive gradient depend upon space velocity and mixture composition. In oxygen mixtures the maximum temperature is found immediately above the cones, and the vertical gradient is a uniform negative gradient for several centimeters.

The maximum observed temperatures in air mixtures show the greatest deviation from the theoretical near the stoichiometric point, being about 20° to 40°C. lower. The maximum temperatures of oxygen mixtures on the average slightly exceed the theoretical. The results are explained on the basis of heat losses, particularly to the grid, and the excitation lag in oxygen mixtures.

The authors wish to thank Doctor Guenther von Elbe for his discussions during the course of this work.

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## FLAME TEMPERATURES IN ENGINES

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Thermodynamic analysis of the transformation of chemical energy into mechanical energy in an internal-combustion engine may be carried out in two different ways. In the first and simplest method of analysis, the energy equation is applied directly to the process, without considering any of the various separate transformations; the engine then becomes a concealed mechanism and its performance is determined by the measurement of external effects. These external effects consist of a flow of gas into and out of the engine, and the transfer of energy in the form of heat and mechanical work to the surroundings. Energy is also transported into and out of the engine along with the gas stream. For this process the energy equation becomes

$$M_2 h_2 - M_1 h_1 = {}_1Q_2 - {}_1W_2$$

where  $M_1$  and  $M_2$  are, respectively, the number of moles of gas entering and leaving the engine,  $h$  is the enthalpy per mole of mixture,  ${}_1Q_2$  is the heat transferred, and  ${}_1W_2$  is the work done. The state of the entering mixture and hence the term  $M_1 h_1$  are usually known, and when any two of the remaining terms can be determined independently, the third term can be readily found from this equation. Such an analysis, while completely rigorous, gives rather trivial information about the performance of an engine, and therefore is of little practical value in considering ways and means of improving this performance.

The second method of procedure is to consider separately each of the energy transformations which occur in the engine and then determine engine performance from the net effect of all these transformations. Such a procedure has the advantage of supplying detailed information about the separate transformations, but does so at the expense of difficult and involved analysis. Thus, while the induction, mixing, and compression of the fresh charge presents little or no difficulty, the transformations during combustion and the early portion of expansion can be treated analytically only after the introduction of a number of simplifying assumptions. In addition, detailed information is required concerning the thermal, chem-

ical, and physical properties of the gases which constitute the working medium. The ultimate test of the validity of these assumptions and the accuracy of these data is the precision with which the state of the gases can be determined at certain points throughout the cycle.

The method of analysis which has just been briefly outlined has been used in the study of ideal, or theoretical, cycles (5, 2, 12, 9) and also in analyzing experimental data from actual engine tests (19). However, before making extensive use of the method, it is very desirable to apply some such test as that just mentioned, in order to form an idea of its reliability and precision. The crucial portion of any internal-combustion engine cycle is that during which chemical energy is being transformed into thermal energy by combustion and thence into mechanical energy by expansion of the heated gas; it is needless to add that this is also the most difficult to analyze. The present discussion is chiefly concerned with the determination of the state of the working medium during combustion and the early part of expansion in an engine operating on the Otto cycle.

#### THE GASES IN AN ENGINE CONSIDERED AS A THERMODYNAMIC SYSTEM

In order to apply thermodynamics to the energy transformations which occur during combustion and expansion in the cylinder of an engine, it is necessary to define exactly the system and the changes of state which are to be considered. The system consists of a mixture of gases, whose state at any instant is completely determined when suitable values can be assigned to the following variables: the total volume,  $V$ , the total pressure,  $P$ , the temperature,  $T$ , and the molal concentrations,  $c_1, c_2, \dots, c_n$ , of each of the  $n$  constituents present. These variables are related by the equation defining concentration as

$$c_i = \frac{m_i}{V}$$

where  $m_i$  is the number of moles of constituent  $i$  in the gas mixture, and the equation of state for a gas, which may be written

$$P = R \cdot T \sum c_i$$

Which of these variables are to be regarded as independent depends upon the particular transformation under consideration. Other properties of the system such as its total mass,  $M$ , its total energy,  $E$ , its total entropy,  $S$ , etc., will also be involved, but these are usually dependent variables. The total volume,  $V$ , unquestionably should be an independent variable, since it is the only one which is always known without ambiguity. Next, in order of uncertainty, is the total pressure,  $P$ , which, if we assume it to

be hydrostatic pressure, can be measured with reasonable precision at any instant during the transformation in question. At this point an important assumption must be introduced before further progress in the discussion is possible.

If definite meaning is to be attached to the temperature and concentrations, it is necessary to assume that the system is homogeneous, all components being in the gaseous phase and the properties either uniform or else varying continuously throughout the region. Therefore the system must either be in thermal and chemical equilibrium and the temperature and concentrations uniform throughout, or else it must be possible to assign to these variables average or effective values, with which are associated values for the total pressure, mass, energy, entropy, etc., which agree with the true values of these dependent variables within satisfactory limits. Such experimental investigations as those of Withrow, Lovell, and Boyd (23), Spanogle and Buckley (21), Erichsen (3), and Rassweiler and Withrow (16) indicate very definitely that the concentrations and temperature are not uniform throughout the gases in an engine cylinder, at least during combustion and the early portion of expansion. Whether or not it is permissible to use average or effective values for the concentrations and temperatures is a problem which will be reserved for later discussion.

Certainly the conclusion is unassailable that, if the application of rigorous thermodynamic analysis to the combustion process can not be accomplished without detailed consideration of temperature and concentration variations, the problem becomes exceedingly difficult. It is true that such analyses as those of Nägel (15), Flamm and Mache (4), Midgley (14), and Rosecrans (18), which take into account the variation of temperature and composition in a gas mixture during combustion, are reasonably satisfactory when applied to combustion in closed spherical or cylindrical vessels. But the oversimplification of the combustion process, which these analyses entail, makes them inadequate when considering the more complicated process of combustion in the cylinder of an engine. For here the volume is very irregular in shape and changing with time, the gases are in turbulent motion, and heat loss to the walls is an important factor. The photographic investigations of Rassweiler and Withrow (17) and of Rothrock (20) furnish convincing evidence of the complexity of the motion of the burned and unburned gas during combustion in an engine, and indicate that a rigorous analysis would probably involve hydrodynamics, with turbulent motion and heat conduction, as well as thermodynamics. Herzfeld (11) has analyzed the combustion and expansion processes in a very complete manner, including the effects of turbulence and heat transfer, but this analysis, even though extremely involved, still

requires numerous questionable simplifying assumptions, for which it is difficult to find experimental verification.

An experimental investigation of gas temperature in the cylinder of an engine was undertaken at the University of Illinois in order to supply definite information with regard to such questions as those which have been mentioned above. The procedure has been to measure the gas temperatures at a series of points in the cycle during combustion and the first part of expansion, and to compare these observed values with values calculated by the method presented by Goodenough and Felbeck (6). Since the results of this investigation have been published previously (10), they will be very briefly reviewed in the present discussion, and attention will be given principally to their interpretation in the light of more recent investigations.

#### MEASUREMENT OF GAS TEMPERATURES IN AN ENGINE

The various methods of measuring gas temperature in an engine have been given detailed consideration in a previous paper (8). Therefore it is only necessary to state that, as a result of such consideration, the spectral-line-reversal method appears to be the only one which may be used satisfactorily to determine these temperatures. The chief advantages of this method, in addition to its simplicity, are the extremely small size and wide dispersion of the thermometric bodies, the radiating atoms, as well as the substantial amount of experimental information which is available regarding the precision and limitations of the method. Erichsen (3) has recently used a spectroscopic method of temperature measurement, in connection with an investigation of combustion in a Diesel engine, for which he claims certain advantages over the line-reversal method. However, the method depends upon the emission of a continuous spectrum of pure temperature radiation which, as the investigations of Withrow and Rassweiler (24) have clearly demonstrated, is not the case in an engine operating on an Otto cycle.

The comparison of the maximum combustion temperature found from line-reversal measurements with those obtained by calculation for a wide range of air-fuel ratios shows rather unsatisfactory agreement (10). Throughout the normal operating range of air-fuel ratios of between 12 to 1 and 15 to 1 the calculated values are approximately 600°F. higher than the measured values, and with both richer and leaner mixtures the difference increases, reaching a maximum of 1000°F. at the lean combustion limit. In order to determine, if possible, the cause of this disagreement, it is advisable to consider some of the different factors which may affect both measured and calculated temperature values.

The factors affecting the measured temperature may be divided into two

groups as follows: (a) Experimental errors inherent in the method of temperature measurement:—non-thermal excitation of radiation from the sodium atoms; absence of thermal equilibrium between the gases and the sodium atoms; cooling effect of the sodium solution entering with the fresh charge. (b) Experimental errors in the method as applied to engine temperature measurements:—deposit or film on the cylinder windows; finite time of stroboscopic shutter opening.

The separate effects of the various sources of error listed above under (a) have been considered in previous publications (10, 8) and, on the basis of the results of numerous investigations of the temperature of stationary flames, the conclusion was reached that the combined effect of these errors could not result in such differences as those found between measured and calculated temperatures. A similar conclusion resulted for the sources of error listed under (b) above. Brevoort (1) has recently made a comprehensive study of the effect of fogging of the cylinder windows on line-reversal temperature measurements, and has found that the deposit which accumulates on the window in 200 min. may raise the apparent temperature by more than 550°F. In the measurements discussed above, however, it was found that mounting the windows flush with the cylinder wall reduced fogging to such an extent that no appreciable error resulted if a lamp-temperature calibration was made immediately after each test.

Therefore it becomes necessary to examine critically the method of calculating the temperatures, for factors which might contribute to the difference between the measured and calculated values. Here again two distinct sources of error exist: (a) Inaccuracies in the method:—incorrect thermal and chemical data for the gases under consideration; disregard of certain dissociation products. (b) Departure of operating conditions from assumed conditions for temperature calculations:—absence of thermal and chemical equilibrium in the gases; departure from adiabatic, constant-volume combustion; temperature gradients in the gases.

The temperature calculations were originally carried out with the specific heat and equilibrium data of Goodenough and Felbeck (6), which were based on the results of calorimetric and chemical experiments. Much more accurate and reliable data, based on spectroscopic experiments, are now available (12, 13). However, the recalculation of some of the temperatures, on the basis of these new thermal data, leaves them practically unchanged. This is due to some rather fortuitous compensating errors in the Goodenough and Felbeck data, which result in nearly the same energy at high temperatures for the two principal constituents, water vapor and carbon dioxide, with either set of specific heat data. Failure to consider the dissociation of  $\text{H}_2\text{O}$  into neutral OH, in the original calculations, was found to lead to temperatures which are about 150°F. too high, but dis-



regarding dissociation into monatomic gases and the formation of oxides of nitrogen had little effect.

The real crux of the matter would appear to be the absence of either thermal or chemical equilibrium. The only satisfactory evidence that the gases are in some kind of stable state is the fact that it is possible to produce a reversal of the spectral line. Whenever there is an insufficient amount of sodium being excited, the dark or reversed line can not be made to appear. Such a condition exists when there is insufficient sodium present in the gases, or when, as during the early part of combustion, only a small amount of the sodium actually present is being excited. When either of these conditions obtains, accurate temperature measurements are impossible. This does not mean that the temperature is uniform throughout the region whenever reversal can be observed; but the reproductibility of the measurements is evidence of the establishment of a definite effective thermal stage in the gases, which exists, with only slight variations, at the same point in numerous successive cycles. von Elbe and Lewis (22) have considered the problem of the thermal equilibrium following combustion in closed vessels, and have suggested that a delay in the distribution of energy over the molecular vibrational degrees of freedom would serve to explain some of the observed phenomena. However, if the sodium atoms are excited by collisions with the heated gas molecules, such an explanation would require that the measured temperatures be higher than the temperatures calculated, assuming complete equilibrium. Kühl (12) discusses briefly the effect of chemical reaction rate on the attainment of chemical equilibrium during combustion in an engine, but advances no experimental evidence, his conclusions being largely speculative.

There remains for consideration the influence of heat loss and temperature gradient on the measured temperatures. In calculating the temperatures the effect of both of these factors was disregarded, but they must certainly influence the measured temperatures. From the temperature measurements of Rassweiler and Withrow (16) it is possible to estimate the magnitude of the temperature gradients which may exist in the gases in an engine cylinder, while from the results of Griffiths and Awberry (7) for reversal measurements with several flames at different temperatures, the effect of temperature gradient on these measurements may be estimated. On this basis it would seem reasonable to add a temperature gradient correction of from 150° to 200°F. to the measured temperatures. Such a correction, together with the lowering of the calculated temperatures by a similar amount, owing to dissociation to form OH, would leave a difference of some 300°F. between measured and calculated temperatures over the normal range of air-fuel ratios. From the results of calculations of heat loss, which were presented in an earlier publication (10), this

would not appear to be an excessive temperature drop to be attributed to heat loss during combustion.

#### SUMMARY

After considering the most likely factors which may influence the measurement and calculation of gas temperatures in an engine during combustion and expansion, there appears to be reasonable agreement between measured and calculated results if (1) temperatures are measured by means of the line-reversal method with suitable corrections for the effect of temperature gradients in the gases, and (2) temperatures are calculated on the basis of thermodynamic analysis, assuming thermal and chemical equilibrium, including the effects of variable specific heat of the gases and dissociation, based on the most recent thermal and chemical data, and correcting for heat loss during combustion.

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# A MOLLIER DIAGRAM FOR THE INTERNAL-COMBUSTION ENGINE

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The limitations of thermodynamics as a tool for studying chemical reactions have been so adequately emphasized in college courses in physical chemistry as to have convinced many automotive engineers that thermodynamic study of the combustion process in an internal-combustion engine can yield no really useful results, that the only way to study knock or combustion mechanism, for example, is to focus attention on experimental studies of rate. The inherent complexity of the thermodynamics of a combustion process carried out at varying total pressure and volume and at such high temperatures as to cause ten different molecular species to be present in appreciable proportions has constituted a further brake on the development of this tool, and the misleading conclusions drawn from oversimplified attacks of the problem have not helped.

Although no claim is made that a thermodynamic study will by itself solve such a problem as engine knock, nevertheless the high temperature level of the combustion process as encountered in engines makes chemical equilibrium more than usually important in relation to rate—and mechanism—studies. Whether a certain combustion process is initiated in a far corner of the chamber ahead of the flame front will depend on the temperature and pressure existing there, which in turn are susceptible of prediction by a thermodynamic treatment of what has occurred in the rest of the chamber. It will be shown that the inherent complexity of a precise thermodynamic treatment of combustion may be reduced to a simple graphical procedure, which will be illustrated by the calculation of the performance of a conventionally "ideal" engine, and by the study of flame movement, temperature, and pressure in an unconventionally "ideal" engine in which combustion occurs during piston movement.

The steam engineer has long been familiar with the use of diagrams representing the thermodynamic properties of steam, and with the advantages of such diagrams for clarifying and simplifying the analysis of the operation of steam power-generating equipment. In the field of internal-combustion engine operation there is the same possibility of use of dia-

grams. If the quantity and atomic composition of a gaseous mixture are specified, the phase rule tells us that the specification of two properties is sufficient to fix completely all the other thermodynamic properties of the mixture. Consequently all the significant properties can be put on a single plot analogous to the Mollier diagram for steam; and the tedious allowance for variation in specific heat with temperature and for shift in chemical equilibrium can be made *once and for all* during the construction of the chart. The solution of such problems as the determination of the maximum possible efficiency of a particular engine cycle is then as simple as the use of the Mollier diagram by the steam engineer. Important differences exist, however, between the plot for steam and for the working fluid of an internal-combustion engine. In the latter there must be a separate plot for each air-fuel mixture ratio of interest. Furthermore, the mixture prior to combustion is in physical but not chemical equilibrium, and separate charts are necessary for the unburned and the burned mixture. The combustion process itself involves a transfer from one chart to the other.

#### DIAGRAMMATIC REPRESENTATION OF THE WORKING FLUID

A survey of the literature proved that the idea of representing equilibrium products of combustion on diagrams was not new. In 1932 Pflaum (14) presented such diagrams plotted with enthalpy and entropy as coördinates; the omission of lines of constant internal energy introduced the necessity for trial and error in many calculations of interest. Pflaum also used thermal data which have since been improved enormously in accuracy, and made inadequate allowance for the complexity of the dissociation process. Subsequent to the completion of most of the present calculations Tanaka and Awano (17) and Kühl (10) have published additional diagrams. Tanaka and Awano followed Pflaum's example in the use of old thermal data, in allowance for dissociation, and in presentation of results on the enthalpy-entropy plane. Kühl, however, used modern fundamental data and made allowance for all important molecular species formed due to dissociation. Although diagrams of the types presented by these authors are of enormous assistance in the calculation of an engine cycle, all of them are characterized by the necessity for a considerable amount of algebraic calculation and of trial-and-error methods of solution.

The thermodynamic properties of interest are temperature  $T$ , entropy  $S$ , enthalpy  $H$ , internal energy  $E$ , pressure  $P$ , and volume  $V$ . Since  $H = E + PV$  one of these latter four could in theory be omitted, but experience in the solution of various combustion problems indicates that freedom from trial and error necessitates including them all. The calculation of the

relations among these six properties requires certain basic thermodynamic data: namely, certain equilibrium constants as functions of the temperature, certain heats of reaction, and the specific heats of the various molecular species as functions of the temperature. The data need not be directly available in just these forms; it is sufficient if these data or certain other data (for example, entropies), related to them by any of a number of thermodynamic expressions, are obtainable.

In recent years the technique of calculating the specific heats of gases over a temperature range extending down to absolute zero has been perfected; the calculations have been carried out for a number of gases, and the results have been published in a series of papers by Johnston and his coworkers (1, 4, 5, 6, 7, 8), and in papers by Kassel (9) and Gordon (2), all of which appeared in the years 1933, 1934, and 1935. Knowledge of the specific heats permits the calculation of entropies; the results of these calculations are given in the papers mentioned. The high precision of the fundamental spectroscopic data used in these calculations and the excellent agreement between these new specific heats and those obtained from recent and refined experimental determinations substantiate the belief that no significant revisions of these values need be expected in the future.

The sources of the internal energy and entropy values for the various molecular species involved in the present work, and the methods used in evaluating changes in internal energy and entropy for the various chemical reactions involved, are summarized in tables 1A and 2A of a previous paper by R. L. Hershey and the present authors (3). The equilibrium constants used are those summarized by Lewis and von Elbe (12).

The fuel chosen as adequately representative of gasoline is octane,<sup>1</sup>  $C_8H_{18}$ ; its hydrogen-carbon ratio, rather than its molecular weight, is its significant characteristic for the present purpose. The air-fuel ratios chosen for study were three, corresponding to a rich mixture (85 per cent of the theoretical air or 117.6 per cent of the theoretical fuel), a mixture in proportion for perfect combustion, and a lean mixture (110 per cent of theoretical air, or 90.9 per cent of theoretical fuel).

The first problem in the construction of a chart of the burned gases is the determination of the composition of a mixture containing carbon, hydrogen, oxygen, and nitrogen, which is in chemical equilibrium at the conditions specified. Because of the high temperature attained in internal-combustion engines, the number of different kinds of molecules existing in important proportions in the products is much larger than in free-burning flames in furnaces. Preliminary calculations indicated that the products

<sup>1</sup> It is recognized that the trend in motor fuel quality is towards lower proportions of paraffinic stock; the difference between  $(CH_{2.25})_x$  and  $(CH_2)_x$  is unknown, but for most thermodynamic calculations it is believed unimportant.

would contain carbon dioxide, water vapor, nitrogen, oxygen, carbon monoxide, hydrogen, OH, H, O, and nitric oxide, the relative importance of the various species depending on the temperature, pressure, and mixture ratio. The method of using data on equilibrium constants to calculate the composition of the products is presented in the reference previously cited (3).

Typical results of such calculations for a total pressure of 800 lb. per square inch on the system are presented in figure 1, showing the effect of temperature on gas composition for each of three mixture ratios (three plots on left). The importance of NO and neutral OH, frequently omitted

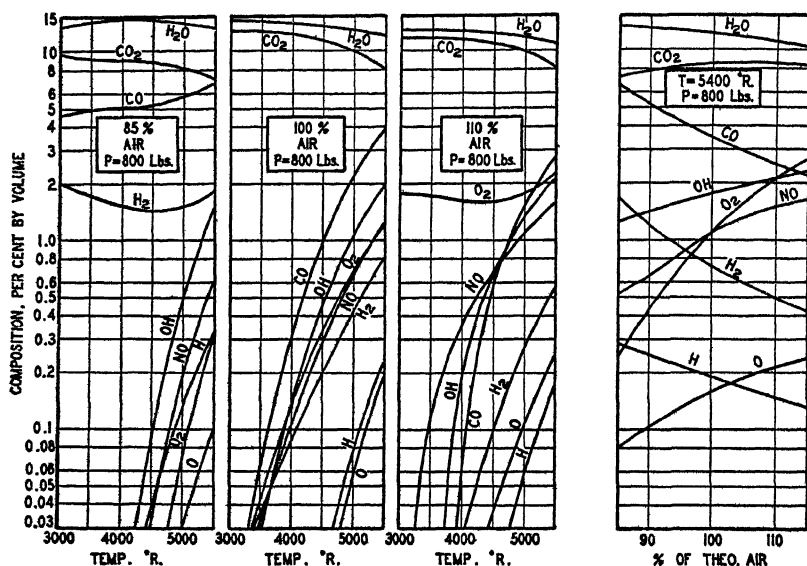


FIG. 1. Effect of air-fuel ratio and temperature on composition of combustion products

from consideration in flame-temperature calculations, and even of atomic oxygen and hydrogen at the highest temperatures, is apparent from a study of the figure. The right-hand plot of figure 1 shows how a variation in air-fuel ratio affects the composition of the equilibrium mixtures, when the temperature and pressure are fixed at 5400° Rankine ( $^{\circ}F. + 460^{\circ}$ ) and 800 lb. per square inch.

With compositions determined for various temperatures and pressures, the next step is the calculation of the various thermodynamic properties fixed by the state of the system, and the presentation of the results on diagrams, one for each mixture ratio under consideration. One such diagram is presented in figure 2, for a rich mixture containing 85 per cent

of the required air for complete combustion (not far from the maximum-power mixture ratio). The material basis for the diagram is the quantity of material (C, H, O, N, in the ten molecular arrangements already mentioned) which contains nitrogen and oxygen equivalent to 1 lb. of air. For figure 2 the weight of carbon plus hydrogen associated with the 1 lb. of oxygen plus nitrogen is 0.0782 lb. Other similar diagrams have been constructed for the lean and the "theoretical" mixture (3).

The thermodynamic properties represented on the diagrams, their symbols, units of measurement, and bases, follow: (1) Temperature,  $T$ , in degrees Rankine or degrees Fahrenheit + 460°; almost horizontal solid lines at 200-degree intervals. (2) Volume,  $V$ , in cubic feet; diagonal solid lines. (3) Pressure,  $P$ , in pounds per square inch; diagonal dashed lines of gentler slope than the volume lines.

(4) Internal energy,  $E$ , in B.t.u., the vertical scale of the diagram. This property is the heat effect attending the conversion, at constant volume and consequently without work, of a mixture from its given condition of composition and temperature to carbon dioxide, water vapor, oxygen, and nitrogen at the base temperature of 60°F. (520° Rankine). Although any path may be chosen in the calculations underlying the construction of the chart, that one simplest to visualize involves cooling the mixture at constant volume to the base temperature, thereby evolving what may be called the sensible internal energy content,  $E_s$ , of the mixture, then allowing the mixture to react at constant temperature and volume to produce only carbon dioxide, water (vapor), nitrogen, and oxygen. The heat evolved along this second leg of the path, the internal energy of combustion at the base temperature, is added to the first quantity to give  $E$ .

(5) Enthalpy or total heat,  $H$ , in B.t.u.; almost horizontal dashed lines found only in the upper portion of the diagram. By definition,  $H = E + PV$  (144/778).

(6) Entropy,  $S$ , in B.t.u. per degree Rankine, the horizontal scale of the diagram. Calculated by assigning zero entropy to carbon dioxide, water vapor, oxygen, and nitrogen at 14.7 lb. per square inch each and 60°F. (520° Rankine). The entropy of any other gas at the base temperature is then equal to its entropy of formation from the preceding constituents of zero entropy. For further quantitative consideration of the entropy concept, essential to an understanding of the technique of calculating the diagrams but not to their intelligent use, the reader is referred to any standard textbook on thermodynamics.

(7) Sensible internal energy,  $E_s$ , in B.t.u. This property already has been defined in the discussion of  $E$ . In the lower temperature range of figure 2, where the chemical composition of the mixture is fixed by tem-



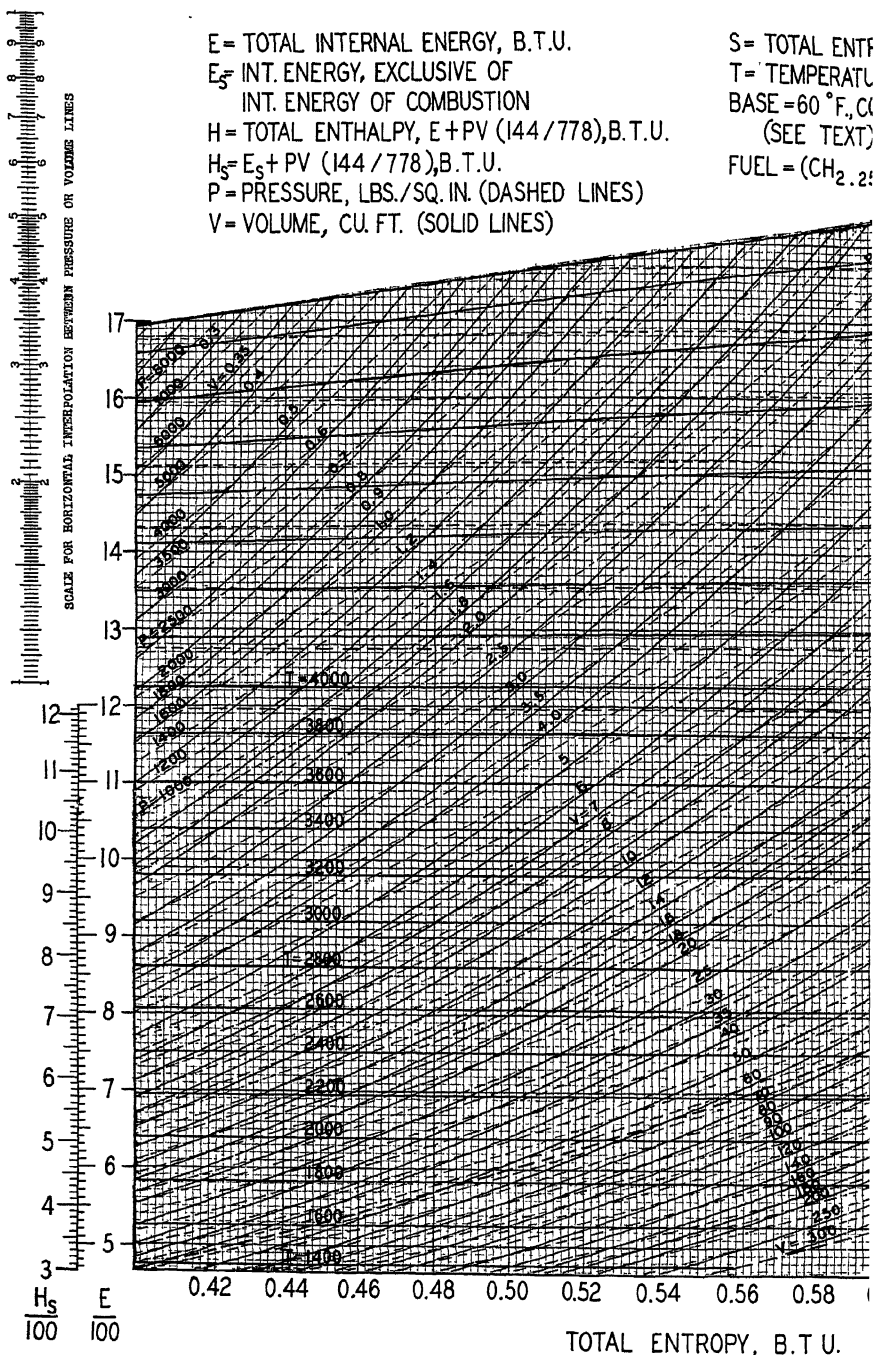
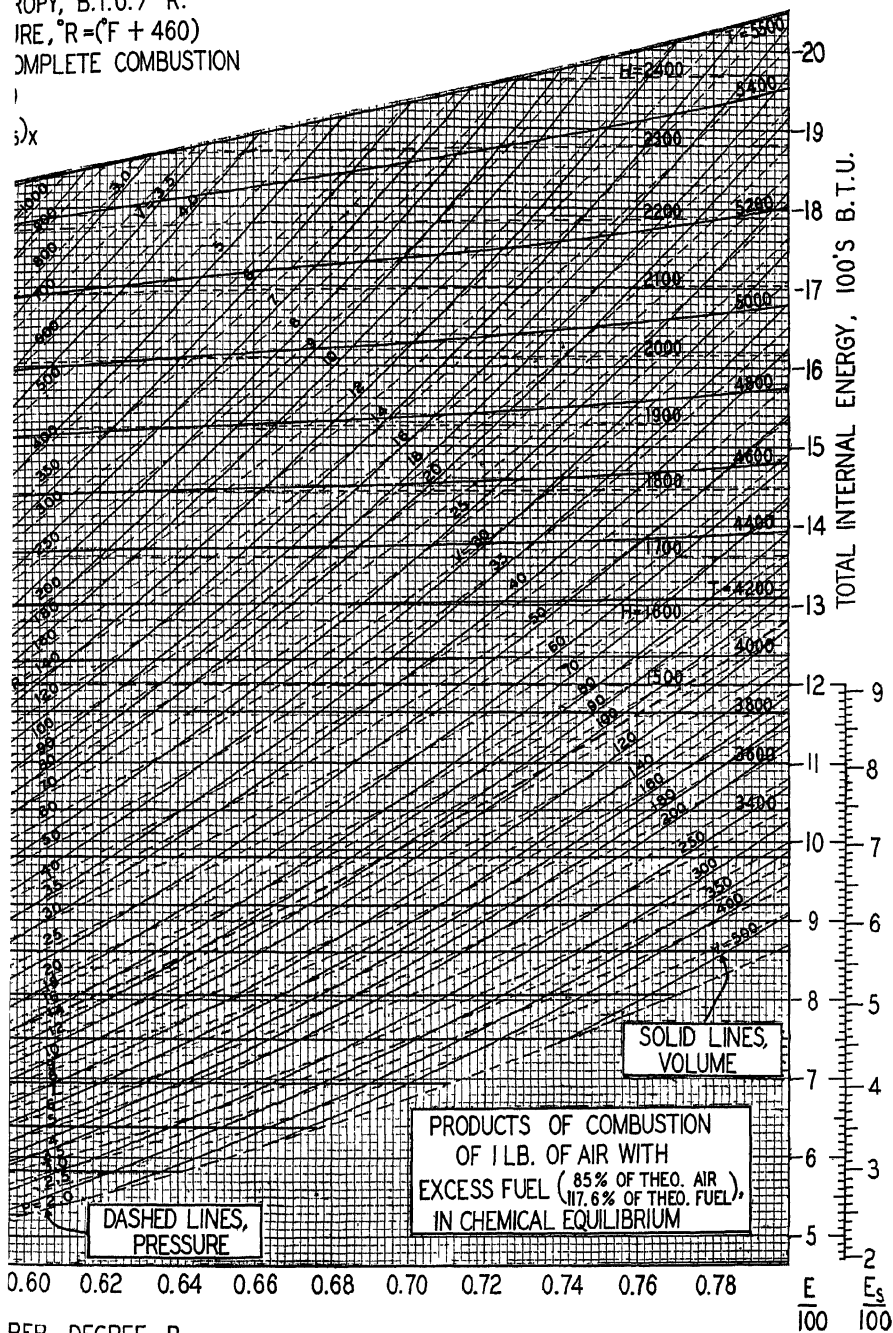


FIG. 2. Thermodynamic properties of the products of combus

ROPY, B.T.U. / °R.  
 RE, °R = (°F + 460)  
 COMPLETE COMBUSTION

1)  
 3)x



perature alone,<sup>2</sup> the value of  $E_s$  is determined completely by  $E$ . Consequently the sensible internal energy is given by the vertical scale on the lower right margin of the diagram, relating  $E_s$  and  $E$ . The difference between  $E$  and  $E_s$  is the internal energy of combustion of the carbon monoxide and hydrogen present by virtue of the insufficiency of air.

(8) Sensible enthalpy or sensible heat,  $H_s$ , in B.t.u. By analogy with  $H$ ,  $H_s = E_s + PV$  (144/778). Like  $E_s$ ,  $H_s$  is a unique function of  $E$  at low temperatures and consequently representable by a scale which appears in the lower left margin of the diagram.<sup>3</sup>

The illustration of the uses of figure 2 in the solution of various problems of combustion in engines must await a discussion of the corresponding diagram representative of the unburned mixture. The mixture prior to combustion consists in part of products of combustion of the preceding cycle, and in part of a mixture of fresh fuel vapor and air. The two parts are, of course, identical in weight percentage of C, H, O, and N. In order that the diagram presenting the properties of the unfired gas shall be on the same material basis as that previously discussed, the basis will again be 1 lb. of oxygen plus nitrogen, and 0.0782 lb. of carbon plus hydrogen. Simple stoichiometric calculations show that this would form 0.0392 lb.-mole if present as combustion products (nitrogen, carbon dioxide, water vapor, carbon monoxide, hydrogen) or 0.0354 lb.-mole if present as air and octane vapor. Let the weight fraction of the mixture existing as unpurged combustion products of the previous combustion cycle be represented by  $f$ , the weight fraction brought in as fresh air and octane vapor by  $(1-f)$ . Then the diagram to be constructed representative of the unfired gas must correspond to a number of moles given by  $0.0392f + 0.0354(1-f)$ , or  $0.0354 + 0.004f$ . The base temperature is 60°F., as before, and the desired thermodynamic quantities, in general, are the same. However, since the diagram is to be used to calculate adiabatic changes that are physically but not chemically reversible, the entropy basis must be defined to omit chemical contributions to entropy; zero entropy is therefore assigned to each constituent at 60°F. (520° Rankine) and 14.7 lb. per square inch. The total internal energy  $E$  is, as before, the sum of two quantities, the sensible internal energy  $E_s$  and the internal energy of combustion  $E_c$  at the base temperature (fuel and products both as vapor). The former is the heat effect attending the constant-volume cooling to the base

<sup>2</sup> Because the only chemical reaction possible is the water-gas reaction,  $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ , which is unaffected by pressure.

<sup>3</sup> It is to be noted that  $(H - H_s)$  is equal to  $(E - E_s)$  and, consequently, to the  $E$  of combustion at the base temperature, not to the  $H$  of combustion. This is a consequence of the choice of basis of the plots, which makes  $E_s$ , not  $H_s$ , zero at the base temperature.

temperature without chemical reaction. Since both the number of moles and the specific heat are very insensitive to variations in  $f$ ,  $E_s$  may be evaluated for some mean value of  $f$  and used with negligible error even though  $f$  varies considerably from the value used.

The internal energy of combustion  $E_c$ , on the other hand, changes greatly with  $f$ . For the rich mixture under discussion  $E_c$  will be  $(1 - f)$  times the internal energy of combustion of 0.0782 lb. of octane, plus  $f$  times the internal energy of combustion of any hydrogen and carbon monoxide in the products of combustion. Taking the lower heat of combustion of octane at constant volume at 60°F. as 19,270 B.t.u. per pound and of the carbon monoxide and hydrogen associated with the products of

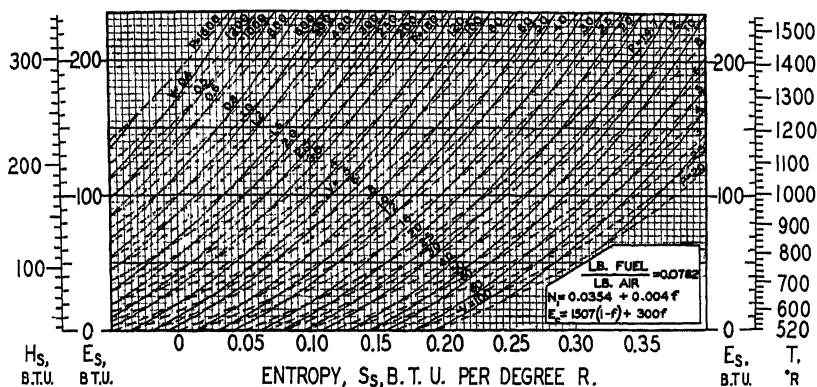


FIG. 3. Thermodynamic properties of a rich mixture of air and octane vapor, plus unpurged combustion products, before firing.  $E_s$  = internal energy exclusive of internal energy of combustion, in B.t.u.;  $H_s$  = enthalpy =  $E_s + PV$  (144/778) in B.t.u.;  $S^s$  = entropy exclusive of entropy of combustion;  $P$  = pressure in pounds per square inch (dashed lines);  $V$  = volume in cubic feet (solid lines);  $T$  = temperature in degrees Rankine ( $= ^\circ\text{F.} + 460^\circ$ ); base = 60°F. (see text); fuel = octane,  $\text{C}_8\text{H}_{18}$ ;  $f$  = weight fraction of charge left in clearance volume (see text).

combustion of 1 lb. of air as 300 B.t.u. ( $E - E_s$  as read from figure 2), the quantity  $E_c$  equals  $300f + (1 - f)19,270 \times 0.0782$ . Since  $E_s$ , but not  $E$ , is substantially independent of the fraction  $f$  of unpurged combustion products in the system, the diagram representative of the unfired mixture, figure 3, is made with vertical scales of sensible internal energy  $E_s$ . The total value  $E$  is obtained by adding to  $E_s$  the internal energy of combustion, readily calculated when  $f$  is known.

Since in the unfired mixture no chemical changes are occurring, the internal energy  $E_s$  is a unique function of  $T$ . Accordingly a scale on the right of the diagram relates these quantities. Similarly a scale on the left relates  $H_s (= E_s + PV$  (144/778)) and  $E_s$ .

The method of using figure 3 representing the unfired gas, referred to

hereafter as the "unburned" chart, and figure 2, referred to as the "burned" chart, will now be illustrated by examples.

#### EFFICIENCY AND M.E.P. OF IDEAL OTTO CYCLES

Let it be desired to study the thermodynamic limitations on power output and mean effective pressure when an Otto cycle engine is operated using octane with 85 per cent of theoretical air, with a compression ratio of 6, the intake and exhaust manifold pressures atmospheric, and the fuel-air mixture leaving the carburetor completely vaporized and at 90°F. Figure 4 represents an indicator diagram for the ideal cycle. Reference to the successive states of the system will be made by appending subscripts corresponding to the numbered points on the diagram. Because of the relation of a cycle to that preceding it, it will be necessary temporarily to assume knowledge of two quantities, and these are most conveniently  $T_1$ , the temperature of the mixture of fresh and unpurged gas prior to com-

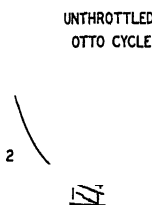


FIG. 4. Ideal indicator diagram for unthrottled Otto cycle

pression, and  $f$ , the fraction of the gas from the preceding cycle left in the cylinder prior to the intake stroke. These will be assumed to be 650° Rankine (190°F.) and 0.05, respectively; they may be checked readily later.

Step 1-2, compression of the charge. On figure 3 the right-hand scale indicates that, when  $T_1 = 650^\circ$  Rankine,  $E_{s1}$  equals 26 B.t.u. On the diagram locate the condition 1, corresponding to  $E_{s1} = 26$  and  $P_1 = 14.7$  lb. per square inch (heavy dashed line). From the diagram read  $V_1 = 16.8$  cu. ft. Since step 1-2 is an adiabatic reversible compression and consequently isentropic, move vertically on the diagram from  $V_1$  to  $V_2$  ( $= 16.8/6 = 2.8$  cu. ft.). From the diagram, read  $E_{s2} = 138$  B.t.u.

Step 2-3, adiabatic combustion at constant volume,  $V_3 = V_2 = 2.8$ . At point 2 the total internal energy  $E_2$  equals the sum of the sensible value  $E_{s2}$  and the chemical value of  $E_{c2}$ , which latter value is  $1507(1 - f) + 300f = 1507 \times 0.95 + 300 \times 0.05 = 1447$ . Then the total  $E_2 = 138 + 1447 = 1585$  B.t.u. Since combustion occurs at constant volume and is

adiabatic, there is no change in internal energy. Therefore,  $E_3 = 1585$  and  $V_3 = 2.8$ , permitting the location of a point on the diagram representing the combustion products in chemical equilibrium, figure 2. For convenience in subsequent use of figure 2, the entropy  $S_3$  will be recorded; it is 0.576.

Step 3-4, adiabatic reversible expansion, therefore isentropic, to  $V_4 = V_1 = 16.8$ . Move vertically downward along the entropy line  $S = 0.576$  of figure 2 from  $V_3 = 2.8$  to  $V_4 = 16.8$ , and read  $E_4 = 1010$ .

Step 4-5, opening of exhaust valve and release of pressure to atmospheric. Although this step is irreversible, if all pressure drop is assumed localized at the exhaust port, then that portion of the charge remaining in the cylinder may be considered to have undergone an adiabatic reversible expansion, doing work on the gas flowing through the port. The condition of the mixture at point 5 then corresponds to point 4' on the dotted portion of the diagram, figure 4. Move down vertically on  $S = 0.576$  of figure 2 to  $P_{4'} = 14.7$  lb. per square inch, the heavy dashed line, and read  $E_{4'} = 723$  and  $V_{4'} = 66$ , and from the scale on the left,  $H_{s4'} = 610$ . These quantities correspond to an amount of material equal to the whole charge, whereas only the fraction  $V_5/V_{4'} = 16.8/66$  or 0.255 of it is left in the chamber.

Step 5-6, expulsion of all but the fraction  $V_5/V_5$  of the remaining gas at constant pressure. This step leaves  $V_6/V_{4'}$  or  $2.8/66$  or 0.0424 of the original charge in the cylinder. This is the fraction  $f$ , assumed to be 0.05 at the beginning of the calculation.

Step 6-1, mixing of the unpurged gas  $f$  with  $(1 - f)$  of fresh fuel-air mixture as the piston moves to bottom dead center. Since this step occurs at constant pressure the total  $H$  is constant, and since no chemical reaction is occurring,  $H_s$  is constant. Therefore the sensible heat of the unpurged residue (which still corresponds in condition to that at point 4' where  $H_s$  equalled 610) plus that of the entering fresh charge must equal that of the mixture at point 1. From figure 3 a fresh charge at 90°F. (550° Rankine) has an  $E_s$  of 6 (right-hand marginal scale) and an  $H_s$  of 43 (left-hand marginal scale).

Then

$$H_{s1} = 0.0424 \times 610 + 0.9576 \times 43 = 68 \text{ B.t.u.}$$

From figure 3, when  $H_s = 68$ ,  $E_s = 23$ , and  $T = 640^\circ$  Rankine.

This constitutes a check on the value originally assumed for  $T_1$ , namely, 650° Rankine. Although this whole calculation could now be repeated with the better values for  $T_1$  and  $f$ , the changes resulting therefrom would be found small; they will be ignored in the present example. The next step is the calculation of thermal efficiency. The work of the cycle is ( $E_2 - E_4$ )

—  $(E_2 - E_1)$  and, since no chemical change occurred between 1 and 2,  $E_2 - E_1 = E_{s2} - E_{s1}$ . The work is, therefore,  $(1585 - 1010) - (138 - 26) = 463$  B.t.u. This work is accomplished by the introduction of  $(1 - 0.0424)$  lb. of fresh air and  $(1 - 0.0424) 0.0782$  or  $0.0749$  lb. of fresh fuel. Adopting the conventional  $H$  of combustion of fuel as the denominator in the expression giving efficiency and using the value 19,240 as the net heat of combustion of octane vapor at constant pressure, one obtains for thermal efficiency,

$$\frac{463}{0.0749 \times 19,240} \times 100 = 32.1 \text{ per cent}$$

The mean effective pressure in pounds per square foot is equal to the net work of the cycle in foot-pounds, divided by the displacement volume in cubic feet:

$$\text{M.e.p., in pounds per square inch} = \frac{463 \times 778}{(16.8 - 2.8) \times 144} = 178$$

For more precise calculation of mean effective pressure or volumetric efficiency it is recommended that  $V_1$  be determined by use of the perfect

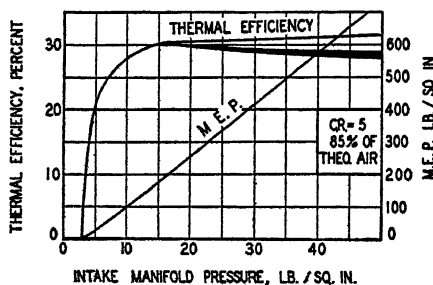


FIG. 5. Effect of intake manifold pressure on the efficiency and mean effective pressure of an Otto-cycle engine

gas law from the known values of  $T_1$ ,  $P_1$ , and  $N_1$  (the number of moles of charge for compression, obtained from  $f$ ):

$$V_1 = 0.729N_1T_1(14.7/P_1) \quad (A)$$

The temperature and pressure at various points in the cycle may, of course, be determined from the charts during the calculation of the efficiency.

The application of thermodynamic-property charts such as figures 2 and 3 has been illustrated elsewhere (3) with numerical examples of the calculation of the performance of various other ideal engine cycles, including throttled, supercharged, variable-cutoff, compression-ignition, and gas turbines. Figure 5, summarizing some of that work, shows the calculated

effect of intake manifold pressure, varied by throttling or supercharging, on the thermal efficiency. The efficiency increases rapidly from zero at 3 lb. per square inch where the pumping loop and work-output loop exactly counterbalance. Above atmospheric intake pressure, the efficiency increases slightly with increased supercharging if the cycle is not charged with the work of supercharging. If the latter work is included, the efficiency drops off slightly at high supercharge pressures, the magnitude of the effect depending on the characteristics of the supercharger. (Isothermal and adiabatic supercharger operation, representing the limiting values, are indicated by two lines connected by a shaded area.) The mean effective pressure, on the same basis as the top curve of thermal efficiency, is shown in the same figure. The mean effective pressure is seen to increase substantially linearly with intake manifold pressure.

#### EFFECT OF FLAME TRAVEL ACROSS THE COMBUSTION CHAMBER

The problem previously considered was simplified to the extent of assuming that combustion took place instantaneously, yielding homogeneous combustion products. Use of the charts will now be made to illustrate the effect, on the pressure-temperature-space-time relations, of the travel of the flame across the combustion chamber. The first example to be considered will be that of combustion occurring at constant total volume (e.g., in a bomb or at top dead center in an engine). Later examples will illustrate the effect of the motion of the piston.

As a flame passes through a confined mass of gas-air mixture the pressure rises continually, the burning of an infinitesimal amount being accompanied by an infinitesimal rise in pressure. Any given element of the gas-air mixture, then, burns at constant pressure or constant enthalpy. As the combustion progresses, both the burned gas behind the flame front and the unburned gas ahead of it are compressed isentropically if no heat is lost. Since flame velocities are low compared to the velocity of sound, the pressure may be assumed uniform throughout the mass. Flame velocities are high, however, relative to the velocities of any eddy currents set up by the passage of the flame, so that mixing should be relatively slight. Furthermore, heat transfer by conduction alone is negligible in the time of passage of flame through a charge. In the limit, then, each element of gas may be assumed to undergo an isentropic compression from its original state as the flame moves towards it, a combustion at constant pressure when the flame reaches it, and a further isentropic compression as the flame moves on into the unburned part of the charge.

A statement of the problem and of the basic assumptions follows: A confined gas-air mixture is ignited and, as the flame is propagated, the total volume is held at a constant value and there is no external heat loss, no



mixing, and no heat flow between adjacent elements of gas. Pressure gradients throughout the mass are negligible. The relations to be found are: (a) the relation between the mass-fraction burned and the pressure, and (b) the temperature distribution through the mass at any time.

#### NOMENCLATURE

The numerical values of all extensive properties are to be those corresponding to the basis of the property charts.

$E_{p_0}$ , in B.t.u. = initial internal energy of unburned gas-air mixture at the original pressure  $p_0$ .

$c$  = mass fraction of the charge burned when the pressure has reached the value  $p_c$ .

$E_{p_c}$ , in B.t.u. = internal energy of the unburned gas-air mixture after isentropic compression from the initial pressure  $p_0$  to the pressure  $p_c$ .

$x$  = mass-fraction position of the element which burned when the pressure was  $p_x$ .

$E_{p_x p_c}$ , in B.t.u. = internal energy of that element of the burned gas at the pressure  $p_c$  which has a mass-fraction position  $x$ , or which has reached pressure  $p_c$  along the path: isentropic compression of the unburned gas-air mixture from the initial  $p_0$  to  $p_x$ , combustion at the constant pressure  $p_x$ , isentropic compression of the burned gas from  $p_x$  to  $p_c$ .<sup>4</sup>

The initial internal energy of the system is  $E_{p_0}$  and, since the combustion is to take place at constant total volume, the internal energy of the entire system must remain constant at this value, although it will be composed of elements having different energies. When the fraction  $c$  of the charge has burned the pressure has risen to the value  $p_c$ , and the internal energy of that portion of the charge as yet unburned will be

$$E_{p_c}(1 - c) \quad (1)$$

The energy of the burned portion of the charge is more difficult to evaluate, since there is a continuous variation in energy throughout it. By the definition of  $E_{p_x p_c}$  the energy of the burned portion is:

$$\int_0^c E_{p_x p_c} dx \quad (2)$$

<sup>4</sup> Note that the single pressure subscript on  $E$  denotes unburned gas and the double pressure subscript denotes burned gas.

The sum of this integral giving the energy of the burned portion and the energy of the unburned portion must equal the constant energy of the system, or

$$E_{p_c}(1 - c) + \int_0^c E_{p_x p_c} dx = E_{p_0} \quad (3)$$

The solution of equation 3 would be extremely difficult without the thermodynamic property charts except by the use of unwarranted simplifying assumptions. Even with the charts its use is difficult without certain working plots which will now be described.

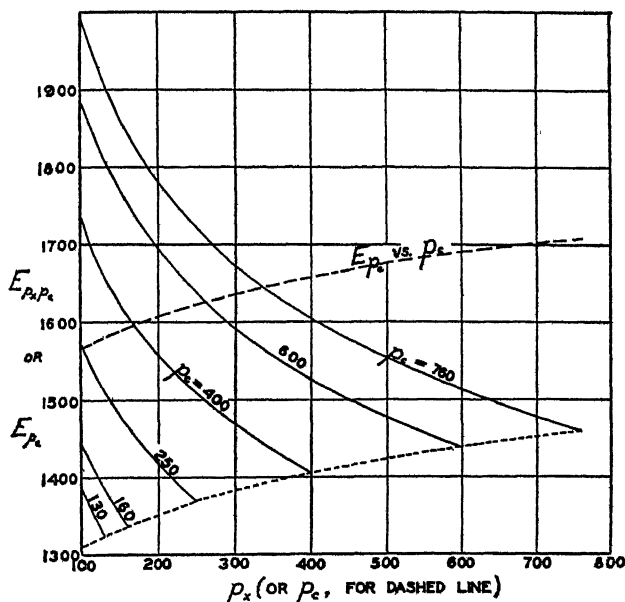


FIG. 6. Relation between  $E_{p_c}$  and  $p_c$  (single dashed line) and between  $E_{p_x p_c}$  and  $p_x$  for different constant values of  $p_c$  (solid lines). (See table of nomenclature.)

Figure 6 presents (single dashed line) the relation between  $E_{p_c}$  and  $p_c$ . The construction of this curve follows simply from the "unburned" chart (figure 3). Since, by definition,  $E_{p_c}$  is the internal energy of the unburned mixture after isentropic compression from its initial state, the intersections of the pressure and energy lines at the entropy of the initial gas-air mixture determine the curve of  $E_{p_c}$  versus  $p_c$ . The "sensible" energy will be read from the chart, and  $E_{p_c}$  is the sum of this value and the energy of combustion.

The family of curves in figure 6 represents  $E_{p_x p_c}$  versus  $p_x$  for various constant values of  $p_c$ . These curves must be obtained from the "burned"

chart, figure 2. The evaluation of any point on these curves must be carried out as described in the definition of  $E_{p_x p_c}$ . At a given pressure  $p_x$ , the properties of the unburned gas are read from the "unburned" chart, figure 3, at the initial entropy. In this case  $H_s$  is the only property of interest. The energy of combustion is to be added to the value of  $H_s$  as read from the chart, giving  $H$ . Since by definition of  $E_{p_x p_c}$  the gas must be burned at the constant pressure  $p_x$ , or the constant value of  $H$  just found, a point may be located on the "burned" chart, figure 2, at these values of  $p$  and  $H$  and the corresponding value of internal energy read. This value is  $E_{p_x p_c}$  for  $p_x = p_c$ . Values of  $E_{p_x p_c}$  for the same value of  $p_x$  and for other values of  $p_c$  may be located by moving along a line of constant entropy from the value just found.

The technique of using equation 3 involves a stepwise calculation with the pressure  $p_c$  chosen as the independent variable. For the first step, if the value of  $p_c$  is chosen not greatly different from the initial pressure  $p_0$ , the value of  $c$  to be found will be small and will be denoted by  $\Delta'c$ . Equation 3 may then be written:

$$E_{p_c}(1 - \Delta'c) + (E_{p_x p_c})'_{av} \Delta'c = E_{p_0} \quad (4)$$

in which  $(E_{p_x p_c})'_{av}$  indicates the average energy of burned gas at the pressure  $p_c$  which burned at pressures varying from  $p_0$  to  $p_c$ . If the step is small and/or if the relation connecting  $c$  and  $p_c$  is substantially linear,  $(E_{p_x p_c})'_{av}$  is the average value of  $E_{p_x p_c}$  as obtained from figure 6 between  $p_x = p_0$  and  $p_x = p_c$  along the curve for the value of  $p_c$  chosen.

For illustration by means of a particular example, consider an engine with a compression ratio of 6.0 operating with a mixture ratio corresponding to 85 per cent of theoretical air and with  $f = 0.042$ ,  $p_1 = 14.7$ , and  $T_1 = 643^\circ$  (from which  $V_1 = 16.5$ ) at the end of the compression stroke ( $V_2 = 2.75$ ); one finds from figure 3 that  $E_{s2} = 138$ ,  $T_2 = 1155$ ,  $p_2 = 160$ ,  $H_{s2} = 220$ ,  $E_2 = 138 + 1507(1 - 0.042) + 300(0.042) = 1594$ , and similarly  $H_2 = 1676$ . Now let the charge be ignited at the conditions just specified, with the piston held at top dead center (volume constant at 2.75) while the flame sweeps through the combustion chamber. The relation between the mass-fraction burned and the pressure, and the temperature distribution through the mass are now to be calculated.

As outlined above, the first step involves the choice of  $p_c$  which, for the present example, will be chosen as 250. From the dashed curve of figure 6,  $E_{p_c}$  (for  $p_c = 250$ ) = 1624. The average value of  $E_{p_x p_c}$  between  $p_x = 160$  and  $p_x = 250$  along the curve labeled  $p_c = 250$  is 1414, which equals  $(E_{p_x p_c})'_{av} \cdot E_{p_0} = 1594$ . Substitution of these values into equation 4 yields  $\Delta'c = 0.143$ , i.e., by the time the pressure has risen from 160 to 250, 14.3 per cent of the charge has been swept by flame.

For the second step equation 4 must be modified to:

$$E_{p_c}(1 - \Delta'c - \Delta''c) + (E_{p_x p_c})'_{av} \Delta'c + (E_{p_x p_c})''_{av} \Delta''c = E_{p_0} \quad (5)$$

in which  $(E_{p_x p_c})'_{av}$  is now to be evaluated between the same values of  $p_x$  but along the curve for the second chosen value of  $p_c$ .  $(E_{p_x p_c})''_{av}$  is then the average  $E_{p_x p_c}$  between  $p_x =$  the first chosen value of  $p_c$  and  $p_x =$  the second chosen value of  $p_c$ , along the curve for the second chosen value of  $p_c$ . Since  $\Delta''c$  is now the only unknown in equation 5, its value can be determined and added to  $\Delta'c$  to give the total  $c$  up to this point.

For each successive step, corresponding new terms in  $\Delta c$  and  $(E_{p_x p_c})_{av} \Delta c$  must be added. It will be noted that each of the terms  $(E_{p_x p_c})_{av}$  will be

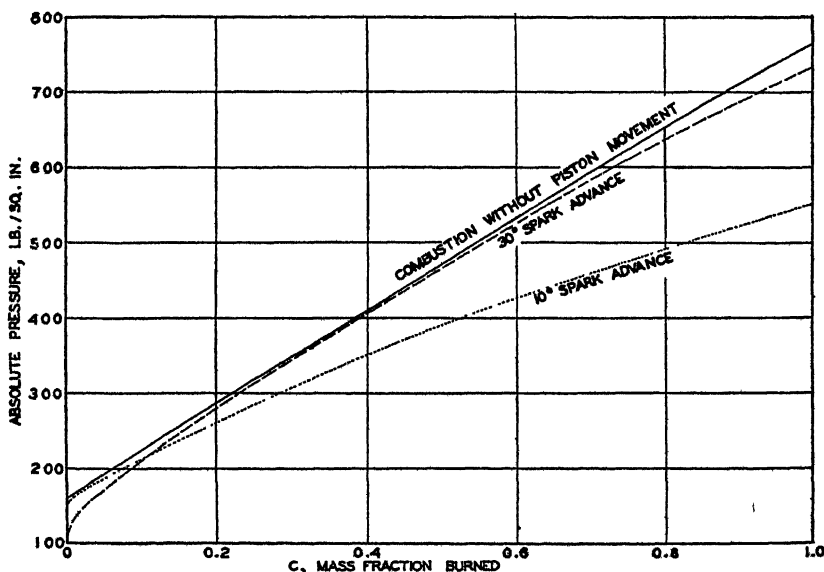


Fig. 7. Change of pressure with progress of combustion for three conditions of firing

obtainable from figure 6 by averaging along the  $p_c$ -curve over the pressure interval within which the corresponding increment burned.

The final results of this stepwise calculation are presented in figure 7 (solid line labelled "combustion without piston movement") as  $p_c$  versus  $c$ . It will be noted that the relation is found to be substantially linear throughout, so that somewhat larger steps could have been taken without appreciable loss in precision. (The literature contains examples of studies of flame propagation based on this simplifying assumption of linearity between  $p_c$  and  $c$ .)

The final pressure is 765 lb. per square inch, a value to be compared with the pressure 775 reached at point 3 in the previously discussed un-

throttled Otto cycle where perfect mixing was assumed at all points. Obviously, if the products of combustion in the present example were thoroughly mixed, at constant volume, conditions would be identical with those at point 3 in the unthrottled Otto cycle example. This mixing would be accompanied by a slight rise in pressure because of the higher specific heat (including dissociation) at the higher temperatures. The phenomenon has been investigated by Mache (13) and by Lewis and von Elbe (11), the latter reporting changes in pressure up to 0.8 per cent for hydrogen-oxygen explosions. The small difference in the pressures indicates that calculations of the type just discussed should be predicated on interest in the temperature distribution through the mass rather than interest in the pressure after combustion. The calculation of the temperature distribution will now be discussed.

The temperature distribution for the present example is presented in the left half of figure 9 as temperature versus mass fraction measured from ignition point. The lowermost curve presents the temperature of the unburned gas ahead of the flame front. The points for this curve were obtained from the "unburned" chart, figure 3, by reading the temperature along the isentropic path as a function of the pressure and obtaining the corresponding mass fraction from the  $p_c$  versus  $c$  plot just discussed. The middle solid curve represents the temperature attained at the instant of combustion of any given layer. Combustion at constant pressure or constant  $H$  provides a means of calculating these points from the corresponding points on the lower curve. The upper curve presents the temperature distribution at the end of combustion. Points for this curve are calculated from the corresponding points on the middle curve by isentropic compression to the final pressure, using figure 2. These curves will be discussed later in comparison with other results. The temperature distributions throughout the charge at various times during the combustion are shown by the dotted lines, the vertical portions showing the position of the flame front.<sup>5</sup>

Part of the technique of making the calculations with allowance for piston movement is the same as that outlined above. Equation 3 (or 4 or 5) is modified only to the extent of correcting the right-hand side for the change in the total energy of the system caused by the work done by the piston. This is simply the average pressure during one of the small steps, multiplied by the change in volume (with the proper sign). Care must be exercised if the piston goes through top dead center in one of the steps. However, equation 4 or equation 5, with the work correction, is not sufficient in this case because the pressure-volume relation is not known in

<sup>5</sup> These results on flame propagation replace those given in figure 7 of reference 3, which were obtained by a method there labelled an approximation.

advance, and hence the work term is not fixed by the technique of choosing  $p_c$ . Additional information related to flame speed—information which no purely thermodynamic analysis can hope to yield—is necessary. The most convenient form that this information can take is relation between  $c$ , the mass fraction burned, and crank angle, readily converted to the relation between  $c$  and chamber volume,  $V$ . With this latter relation given, the calculation for a single step of the combustion process involves trial and error in finding those values of  $\Delta c$  and  $\Delta V$  which will satisfy both equation 4 (or 5), with the work term included, and the  $c$ - $V$  relation.

For illustrative purposes two examples have been calculated, with ignition  $30^\circ$  and  $10^\circ$ , respectively, before top dead center. In both cases combustion was assumed to have been completed in  $40^\circ$  of crank revolution. As a fair approximation the fraction burned was assumed proportional to

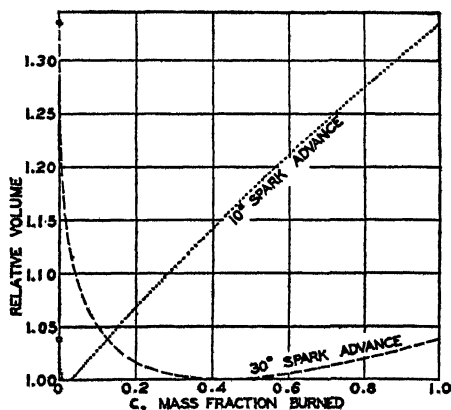


FIG. 8. Progress of flame in relation to piston movement

the cube of the time after ignition, or to the cube of the crank travel after ignition. This approximation was combined with the known relation of volume to crank angle to produce the curves of figure 8, giving the  $c$ - $V$  relation for the two cases in question. Admittedly the relations presented in figure 8 represent an assumption, although data presented by Rassweiler and Withrow (15) indicate that pressure is nearly cubic in time. The assumptions do not detract from the value of the examples as illustrations of a method.

The stepwise-calculated relations of pressure to fraction burned are presented in figure 7 as the dashed and dotted lines. Since ignition occurs before top dead center has been reached, combustion starts at a lower pressure than in the previous example. During the early stages of combustion the pressure rise is more rapid than in the previous example, by virtue of the combined effects of combustion and compression by the

piston. Beyond top dead center, however, the expansion resulting from piston movement causes a decrease in the slope of the curves. This latter effect is particularly pronounced in the example with  $10^\circ$  spark advance, since nearly all the combustion occurs during the expansion stroke.

With the relation of pressure to fraction burned known, the calculation of the temperature distribution curves presented in the right half of figure 9 is as described in the first example. These curves show clearly the in-

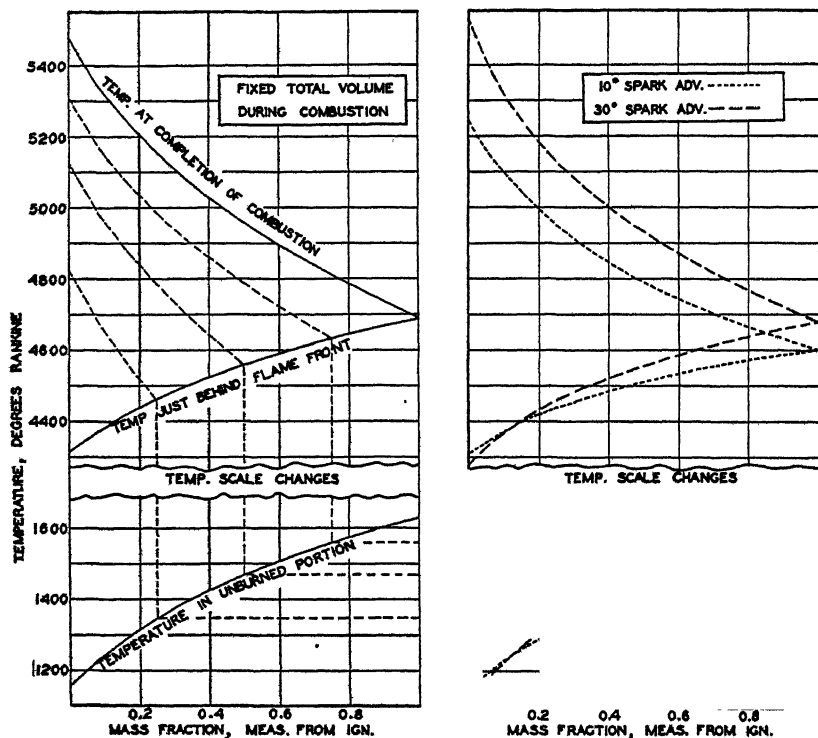


FIG. 9. Effect of flame travel on temperature in a combustion chamber. Left—chamber of fixed volume; right— $30^\circ$  and  $10^\circ$  spark advance, with flame travel occupying  $40^\circ$  of crank revolution.

crease in temperature caused by advancing the spark. Of particular interest are the two lowermost curves, which represent the temperature in the unburned portion into which the flame is advancing. Near the end of combustion the temperature of the unburned gas is about  $100^\circ$  higher when the spark advance is  $30^\circ$  than when it is  $10^\circ$ . This temperature difference, alone or in conjunction with the large pressure difference occurring simultaneously, undoubtedly affects the nature of the reactions ahead of the flame front where "knock" probably starts. It is to be noted

also that the usually calculated compression temperature is that at  $c = 0$ , which is several hundred degrees lower than the actual temperature in the later stages of combustion.

Experimental studies of the variation in flame temperature across an engine head confirm the general character of the upper curves of figure 9. Rassweiler and Withrow (16), using the sodium D line reversal method to measure temperatures in an engine operating with open throttle with 80 per cent of theoretical air and a compression ratio of 4.4, found the temperature at the firing end to rise from  $4200^{\circ}\text{R.}$  (at  $10^{\circ}$  of crank revolution after firing) to a peak of  $4800^{\circ}\text{R.}$ , under non-knocking conditions.

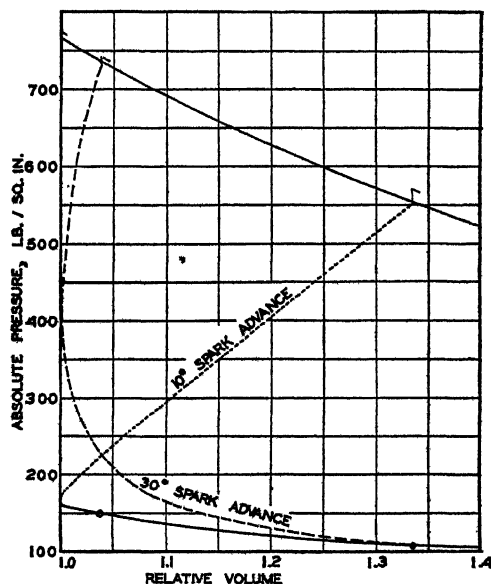


FIG. 10. High-pressure end of indicator card for conditions of figure 9. (Note: zero of  $P$  and maximum  $V$  not shown.)

Calculations following the method of the present paper, with the simplifying assumption of all combustion occurring at top dead center, indicated temperatures at the spark plug of  $4220^{\circ}\text{R.}$  and  $5250^{\circ}\text{R.}$  at the start and completion of combustion, respectively. That the latter value is considerably in excess of that obtained by experiment is to be expected, since the time of combustion was not zero, but approximately  $40^{\circ}$  of crank revolution.

The relation of pressure to total chamber volume, for the three examples considered, was obtained by combining the  $V$ - $c$  and  $p$ - $c$  relations of figures 7 and 8. The results are presented in figure 10, which represents an enlargement of the upper corner of the calculated indicator cards for the



three cases. The solid curve, part of which is the left edge, corresponds to combustion at top dead center. It is to be noted that the area of the card for 30° spark advance is only slightly less (about 2 per cent) than that of the conventionally "ideal" cycle; an important conclusion is that the simplification of calculations of the efficiency of various engine cycles by assuming combustion at top dead center, does not lead to any great error. The area of the indicator card for 10° spark advance, however, is much less than that of the others. According to figure 10 it is approximately 40,000 ft.-lb. or 51 B.t.u. less than the "ideal" cycle. The latter cycle, according to the first example discussed, yields a work output of 463 B.t.u., from which one concludes that retarding the spark advance from 30° to 10° is accompanied by approximately 10 per cent loss in efficiency.

#### SUMMARY

Quantitative calculations of the effects of flame propagation and of piston movement on the temperatures attained in the various parts of on Otto-cycle engine charge during combustion are made relatively simple by the use of a Mollier diagram of the properties of the combustion products of octane and air. The method is applied to a consideration of the effect of spark advance on the temperature attained ahead of the flame front, and it is concluded that the results are significant in studies of engine knock.

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